ENGR-CIVIL
ENGR-CIVIL

VOLUME XXXVII JANUARY, 1958 No. 1

OHIO STATE UNIV
FEB 3 1958
L

FUEL

A QUARTERLY JOURNAL OF FUEL SCIENCE

Editor
SIR ALFRED EGERTON, F.R.S.

Deputy Editor (U.S.A.)
C. H. RUOF

Editorial Committee

I. G. C. Dryden
F. H. Garner, O.B.E.
R. H. Griffith
W. Idris Jones, C.B.E.
J. R. Joyce
J. G. King, O.B.E.
R. Lessing
D. M. Newitt, F.R.S.
A. Parker, C.B.E.
M. W. Thring

BUTTERWORTHS SCIENTIFIC PUBLICATIONS
LONDON

XUM

The following articles were published in the December issue of **COMBUSTION AND FLAME,** *the new Quarterly Journal of the COMBUSTION INSTITUTE*

	Page
MECHANISMS FOR THE FORMATION OF IONS IN FLAMES. *H. F. Calcote*	385
STUDIES ON THE OXIDATION OF HYDROCARBONS UNDER EXTREMELY CLEAN EXPERIMENTAL CONDITIONS. *Z. G. Szabó and D. Gál*	404
DETERMINATION OF BURNING VELOCITY OF PENTABORANE–OXYGEN–NITROGEN MIXTURES. *W. G. Berl, E. L. Gayhart, E. Maier, H. L. Olsen and W. T. Renich*	420
AN ISOTOPIC TRACER STUDY OF CARBON FORMATION IN HYDROCARBON FLAMES. *R. E. Ferguson*	431
A THEORY OF FLAME PROPAGATION LIMITS DUE TO HEAT LOSS. *E. Mayer*	438
EXTINCTION OF FIRES IN LIQUIDS BY COOLING WITH WATER SPRAYS. *D. J. Rasbash and Z. W. Rogowski*	453
INTERPRETATION OF THE SAMPLE TAKEN BY A PROBE IN A LAMINAR CONCENTRATION GRADIENT. *A. A. Westenberg, S. D. Raezer and R. M. Fristrom*	467
RECENT DEVELOPMENTS AND NOTES. *W. A. Kirkby*	479
PUBLICATIONS	487
INDEX	489

FUEL

A Quarterly Journal of Fuel Science

Editorial The customary Editorial in the January issue of *Fuel* began last year with an account of the decision which had been taken to publish a quarterly Journal, *Combustion and Flame*, in parallel with *Fuel*, the quarterly *Journal of Fuel Science*. The new Journal was to become and has become the official quarterly of the Combustion Institute. The first number of the new Journal was issued in March and other numbers appeared in June, September and December.

Fuel has not suffered from the change, in fact its pages are still barely sufficient to keep pace with the inflow of communications which come from all parts of the world. Page space is therefore valuable and my editorial this year will be briefer than usual. It will be helpful, too, if authors will remember that the shorter and more succinct they can make the presentation of their work the easier it becomes to diminish delays in publication.

Particular attention is drawn to the pamphlet which was issued and circulated along with the April issue of the Journal to guide authors in the submission of their communications to the Journal and to help in the preparation of papers.

Readers will have noted that the titles of papers published in the Journal *Combustion and Flame* are given on the cover of the subsequent issue of *Fuel*. A list of papers along with authors' names, which have been accepted for publication in future issues of *Fuel*, is now also provided. Reference was made to the appointment of Dr Ruof as Deputy Editor for communications emanating from the U.S.A., in a special Editorial last April. Dr Kirkby's Notes referring to recent developments and the Notes, provided by the Overseas Correspondents, of fuel developments in their respective countries form features which the Editorial Committee feel sure are helpful to readers of the Journal. We are greatly indebted to the authors of these Notes.

The report of the Commission appointed by the Organization for European Economic Cooperation to study Western Europe's energy needs was reviewed in last year's Editorial and further in Dr Kirkby's Notes (pp 114, 115). Attention was drawn to the conclusion that coal will be the main source of energy for many years yet and that Western Europe need not fear investment in its coal industries which need to be expanding. The same applies to several other regions of the world, in spite of the increasing incursion of oil as a source of energy and the prospect of considerable and increasing supplies of energy from nuclear sources. The world's population is increasing (at the rate of an addition of 70 000 per day). Standards of living are rising in many parts of the world. Energy supplies have not only to keep pace, but be ready to meet demand. Coal for some time to come will be the mainstay.

One has only to glance at the titles of the communications to *Fuel* to realize that as knowledge of the constitution of coal increases, so the problems which arise also grow. Coals from different regions of the world and even from the same seam vary in various respects and it is likely that in this branch of fuel science research will continue to be very active. As knowledge of the constitution of coal becomes more precise, so the problems connected with cleaning, drying, carbonization etc., all become more amenable to scientific investigation.

Coal is not alone amongst natural fuels. There is much that has to be learnt about the constitution of other fuels, such as peat, and their changes on heating. There are many problems relating to the constitution of oil fuels. We were glad to receive Dr Waterman's paper on the application of sound velocity measurements for the study of the constitution of oils. There are special fuels needed to propel satellites and other missiles and no doubt in future we may expect to receive papers relating to the constitution and behaviour of such fuels.

The scenes are changing rapidly, but energy is the basis of all activity. The more that is known about the nature of the sources of energy, the less wastefully can the valuable natural resources be used. Eventually it may come to be realized that it is a waste of nervous energy to wrangle over such resources as there are or may be, and that it is better to study closely the world's needs and to arrange for their equitable satisfaction for the common good with as much sense and with as little sensation as possible.

A. C. Egerton

Studies in Bomb Calorimetry VIII—Design of Calorimeter Systems

R. A. MOTT

The principles enumerated in Part VII are applied to systems using static, isothermal and adiabatic jackets. For static jackets, it is shown that the specification of the water capacity is inadequate but that the specification of the maximum temperature change during a determination is satisfactory. The covers of a calorimeter vessel, for both static and isothermal systems, should be designed to minimize the effect of changes of air temperature, this being simpler and cheaper than thermostatically controlling the calorimeter room. The calorimeter vessel should be so designed as to make the effective heat capacity of the system substantially independent of temperature over any reasonable range. For an isothermal system, it is shown how the speed of stirring affects repeatability and how the length of the chief period can be fixed on a basis of best repeatability; a standard deviation of 0·075 per cent has been attained in determinations of effective heat capacity using a resistance thermometer. The development of the design of adiabatic calorimeters is traced and their value shown to be the attainment of conventional accuracy whilst reducing the time of a determination to about one third of that required with other systems; the precautions necessary to ensure good performance are described.

IN Part VII[1] of this series certain basic principles for the design of bomb-calorimeter systems were deduced; the application of these (and other) principles is discussed in the present paper. It was shown (loc. cit.) that the rate of cooling in a calorimeter depends upon the rates of heat loss due to conduction, convection, radiation, evaporation and stirring and that, by good design, each of these may be either eliminated, made constant or made to conform to Newton's law of cooling, so that an accurate cooling correction may be applied. The outstanding observation was that, in calorimeters used for the routine calorimetry of fuels, evaporation is a more important factor than has hitherto been appreciated, partly because in studies of special calorimeters, such as those devised for the determination of the calorific value of 'standard' benzoic acid, internal evaporation is usually eliminated by completely filling the calorimetric vessel with water and sealing it: the effect of evaporation is limited, in such calorimeters, to that due to actual loss of water vapour from the system, which can be prevented by suitable sealing devices. In calorimeters used for routine calorimetry, it is not usually considered practicable to fill the calorimeter vessel completely with water and the resultant air space becomes saturated with water vapour which can condense on the inside cover of the calorimeter, and, where such a cover is not used, on the inside of the water jacket; loss from the system can, in general, also occur.

As shown in Part III[2] of this series, errors which are not accounted for by the cooling correction do not influence the result of a calorific value determination provided that the total heat release is approximately the same as in the determination of the effective heat capacity and that the magnitude of the errors remains unchanged. To ensure the latter, the essential factor

in accurate routine calorimetry is the reproduction of the 'standard' thermal conditions of the determination of the effective heat capacity. To this end, there is a tendency for manufacturers to adopt the type of calorimeter which has been invariably used for the accurate determination of the calorific value of benzoic acid, namely, an 'isothermal' system in which the jacket is thermostatically controlled at a specified temperature. Another type of system is the 'adiabatic', in which an attempt is made to maintain the jacket at the same temperature as that of the calorimeter, so that, ideally, a cooling correction need not be applied and the time required to carry out a test is reduced. The system commonly used hitherto may be termed the 'static' type, in which a large water-jacket, usually unstirred, is used to insulate the calorimeter proper from external heating effects. It will be convenient to discuss the design of systems under the headings of these three descriptive terms for the type of water-jacket used.

STATIC SYSTEMS

Design of the jacket

In *Fuel Research Survey Paper No. 7*[3] (1927) it was recommended that the water-jacket 'should contain not less than 20 litres of water to provide an environment of sufficiently constant temperature to ensure an accurate radiation correction', but the advised volume was reduced to '15 to 20 litres' in *Survey Paper No. 44*[4] (1940). In *B.S. 1016: 1942*[5] it was stated that the 'water capacity of the outer jacket shall not be less than five times that of the total water equivalent of the calorimeter'; since the total water equivalent is of the order of 2 500 g, this means that the capacity of the jacket should be at least 12½ litres. A similar guide is given in the German standard *DIN 51708*[6] (1950). In A.S.T.M. standards[7, 8] no characteristic of the water-jacket is specified, except that the temperature shall be within 2 or 3°C of that of the room and that the jacket shall be stirred continuously.

In the course of the work described in Part VII[1] of the series, observations of the calorimeter, jacket and air temperatures (t_c, t_j and t_a, respectively) were made throughout a number of determinations, which were usually continued for at least 15 min after firing. It is useful to arrange the data to show the mean change in temperature of the water in the jacket during a calorimetric determination in relation to the difference between the temperatures of the jacket and the air. It is preferable to confine the study to the 15-min period commencing 1 min after firing: during the fore-period (before firing) and the first minute after firing heat is usually lost from the jacket to the calorimeter, whereas, subsequently, the heat flow is usually from the calorimeter to the jacket. The results are summarized in *Table 1*.

It will be observed that, so long as $(t_j - t_a)$ is within the range $-1{\cdot}0$ to $4{\cdot}0$°C, the mean change in the jacket temperature over the period defined is small for all four systems and the maximum change rarely exceeds $0{\cdot}10$°C, so that the temperature of the water in the jacket is substantially constant during a calorimetric determination. If, however, $(t_j - t_a)$ is within the range $4{\cdot}1$ to $6{\cdot}5 \pm 1{\cdot}5$°C, in systems 1, 2 and 4 the temperature of the jacket alters to a much greater extent during the 15-min period chosen, and the maximum change is no longer negligible. In system 3, which is thermostatically controlled, the observed change in jacket temperature is less than

for the other systems, the order being the same as for lower values of $(t_j - t_a)$, showing the effectiveness of the control.

It can be concluded that the capacity of the water jacket is not a good guide to use in the specification of its desirable characteristics, for system 4 (with a water jacket of only 3·65 l. capacity and with surrounding insulation)

Table 1. Change in jacket temperature during 15-min period for different jacket temperatures

System*	Jacket capacity (l.)	Jacket temperature − air temperature: $t_j - t_a$(°C)					
		−1·0 *to* 1·0		1·1 *to* 4·0		4·1 *to* 6·5 ± 1·5	
		Change‡ in jacket temperature (°C)					
		Mean	*Max.*	*Mean*	*Max.*	*Mean*	*Max.*
1	20·6	0·03	0·08	−0·03	−0·08	−0·11	−0·26
2	20	−0·01	−0·11	−0·01	−0·11†	−0·11	−0·24
3	13	0·03	0·07	−0·02	−0·10	−0·01	0·05†
4	3·65	—	—	−0·02	−0·08	−0·23	−0·33

* Systems 1 and 3 are the same as those of Part VII: No. 1 is the Gallenkamp–Krocker calorimeter with a reciprocating stirrer and a single cover on the jacket; No. 3 is the B.C.R.A. Isothermal calorimeter with the acket thermostatically controlled and double covers separated by an insulating layer. System 2 is that which preceded Systems 2a and 2b of Part VII; it had double covers, separated by a 3 in. air space, and a rotary stirrer. System 4 is the B.C.R.A. Adiabatic calorimeter (see later) used as a static-jacket system; the small jacket is surrounded by a wooden box, with an air space between.
† Neglecting one test (the first of the day) in each case.
‡ Positive sign denotes increase.

was as effective as the other systems for $(t_j - t_a)$ between 1·1 and 4·0°C. It is preferable to characterize the jacket by its ability to maintain a temperature within certain limits. By postulating that, for a system with a cooling constant $[K = (v'' - v')/(t'' - t')$, where t' and t'' are the mean temperatures in the fore- and after-periods, respectively, and v' and v'' are the mean rates of cooling in these periods] of 0·0020 min^{-1}, K should be constant to within ± 0·0001 min^{-1}, it can be shown that the change in jacket temperature during a determination should not exceed 0·15°C, and that if $K = 0·0030$ min^{-1} the change should not exceed 0·10°C. It is desirable, therefore, to specify that the insulating ability of the jacket should be such that the temperature in it will not vary by more than 0·15°C during a determination. This can be achieved by making the jacket of a certain minimum capacity or by the use of external insulation.

With a 20 l. capacity jacket, about 6 l. of this are usually under the bottom of the calorimeter vessel; with a bench below, heat exchange via the base is much less likely than through the side. It is desirable that most of the jacket space below the calorimeter vessel be dispensed with, this step permitting a reduction in height (as for System 2b, Part VII) and leaving most of the capacity in an annular ring round the calorimeter vessel. The reduction in height brings the thermometer more conveniently to eye level.

Design of the calorimeter covers

In Part VII it was stated that the temperature of the jacket is influenced more by change in air temperature than by heat exchange from the calorimeter. An analysis has been made of the change in air temperature, during a 15-min period, in a small calorimeter room facing south. The results are summarized in *Table 2*.

The bias of the change is in the direction of an increase in temperature. A change of 1·25°C is a 1 in 100 chance, but a change of 1·0°C is a 1 in 20 chance.

The rate of cooling of the calorimeter may be expressed by the general equation

$$v = a(t_c - t_j) + b(t_j - t_a) + c \ ^\circ\text{C/min} \quad \ldots . [1]$$

For System 1 (Part VII), the coefficient b was 0·00055, so that the mean observed change in atmospheric temperature of 0·18°C will just influence

Table 2. Change in air temperature during a 15-min period

Number of observations	15
Mean increase in 15 min	+0·18°C
Standard deviation	0·42°C
95 per cent limits	−0·64 to 1·00°C
99 per cent limits	−0·90 to 1·26°C

the cooling constant of this system by 0·0001 min^{-1} when $(t_c - t_j)$ is 1°C. Thus the room would be unsuitable for use with System 1.

It is desirable that the design be altered so that the system is uninfluenced by any reasonable change in $(t_j - t_a)$ which may be expected. The requirement is that coefficient b (equation 1) be not more than 0·0001, so that a change of $(t_j - t_a)$ of 1·0°C (the 1 in 20 chance) changes K by 0·0001 min^{-1}. This is achieved by the use of double covers with an insulating layer between, as described in Part VII.

It should be noted that changes in air temperature are often sudden, and may be due either to the emergence of the sun from behind a cloud (in a room facing south), or vice versa, or to the door of the room being opened. It has been observed that such sudden changes most commonly occur during the first test of the day. With a well designed calorimeter, the only additional precautions necessary to ensure negligible effect of air temperature are the shielding of the calorimeter from direct sunlight and draughts. Further, it is usually cheaper and easier to modify (if necessary) the cover system and to take the additional steps mentioned than it is to introduce effective thermostatic control of the room.

Design of the calorimeter vessel

The function of the calorimeter vessel is to hold the bomb and some 2 l. of water. It must be insulated from the water-jacket, must be capable of being easily removed, emptied and refilled after each determination, and, in being replaced, should be capable of easy location in the jacket. It has been customary to make it of brass sheet, but this is soft and easily dented by accidental knocks. Most makers have preferred to make it of cylindrical shape, but this, though the easiest for fabrication, does not readily allow for the use of a rotary stirrer. If made of thin-gauge material, it is usual to strengthen the top with a wire, round which the lip is rolled. Such a design, however, does not lend itself to the use of a cover of the type which has been shown to be desirable.

It was shown in Part III[2] that the effective heat capacity of a calorimeter system could be constant (say, $\pm$ 1 cal/°C) by judicious design, so that, for an increase in working temperature (mean of temperatures on firing and at the end of the chief period), the increase in the heat capacity of the metallic parts of the system balanced the decrease in heat capacity of the water (for which the specific heat decreases with increase of temperature within the working range). The most convenient balance was obtained by the use of 2 l. of water and a value of ($M_S + M_B/4$) of 3 kg, M_S and M_B being the weights (respectively) of the steel parts and the brass and bronze parts of the calorimeter; the effective heat capacity was then constant (the modulus of the factor for correcting to 25°C being not greater than 0·5 cal/°C) over the range 12·7 to 27·9°C. A B.C.R.A. bomb (Part V[9], *Figure 8*) of 330 ml capacity has a total weight of 2·45 kg (the aluminium bronze nut weighing 0·5 kg). If the calorimeter vessel is made of 16 gauge brass (to give a rim sufficiently stiff to receive a cover) it weighs *c.* 3·9 kg; if it is made of Monel metal, 22 gauge is a satisfactory thickness and the weight is *c.* 1·5 kg. With a brass stirrer of 0·05 kg, the alternatives (making due allowance for Monel and aluminium bronze) are:

With 22 gauge Monel metal calorimeter vessel	$\dfrac{M_S + M_B/4 \text{ (kg)}}{3{\cdot}4}$
With 16 gauge brass calorimeter vessel	3·2

Thus in both cases the 'effective weight' of the system is about 3 kg and the effective heat capacity is substantially independent of temperature over any reasonable temperature range.

The use of Monel metal (or stainless steel) is preferable to brass because of the higher yield point (giving greater resistance to distortion by accidental knocking or dropping) and lower weight. All calorimeter vessels should have the lifting handle set sufficiently below the upper rim to allow for the insertion of a cover.

The calorimeter vessel should be supported in the air space on insulating pins fixed to the jacket; the height of the pins should be such as to give the desirable 1 cm air space. A cork mat should not be used. Three pins give satisfactory support, each engaging with an indentation in the base of the calorimeter vessel. Ebonite is a satisfactory material and the total contact area should preferably be of the order of 1 cm^2.

A cylindrical calorimeter vessel with a stirrer which has to be inserted and withdrawn once per determination is not so convenient to the operator as a design in which the stirrer remains within the vessel and is engaged by a clutch on fitting the covers. To this end, a vessel of pear- or egg-shaped horizontal section is convenient, the narrow portion forming the convection tube for the (rotary) stirrer.

ISOTHERMAL SYSTEMS

The calorimeters used for determining the calorific value of benzoic acid have all been of the isothermal type (e.g. refs. 10, 11), the water in the jacket being stirred, heated to a specified temperature by thermo-elements and controlled

XUM

thermostatically. Isothermal calorimeters are now being manufactured and sold for routine fuel calorimetry. The heating and control can be achieved in a variety of ways. Most systems employ two heaters, one of large capacity for initial heating and the other, of low capacity, for control. Two stirrers are also usually used, this being desirable to ensure good mixing in the annular jacket. In the prototype of the Griffin–B.C.R.A. Isothermal calorimeter an electronic control system was used and the temperature in the jacket could be maintained constant to within $\pm 0{\cdot}006°C$. This is, however, an unnecessary refinement and it is sufficient to maintain the temperature in the jacket constant to within $\pm 0{\cdot}06°C$ by means of a mercury-contact thermometer.

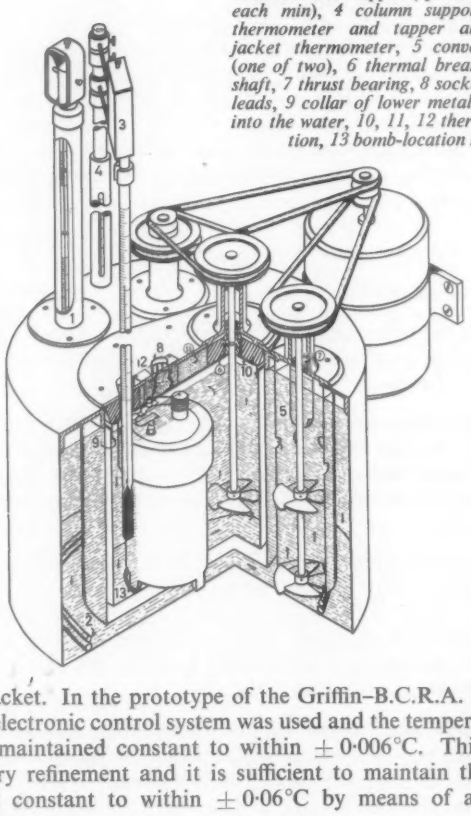

Figure 1. Griffin–B.C.R.A. Isothermal calorimeter showing: 1 contact thermometer for thermostatic control of jacket, 2 main and auxiliary heating coils, 3 thermometer tapper (operates for 10 sec each min), 4 column supporting vessel thermometer and tapper and housing jacket thermometer, 5 convection tube (one of two), 6 thermal break in stirrer shaft, 7 thrust bearing, 8 socket for firing leads, 9 collar of lower metal lid dipping into the water, 10, 11, 12 thermal insulation, 13 bomb-location ring

Calorimeter jacket

Since the jacket is thermostatically controlled, the specification of the details of design is of less importance than for the static type. In the Griffin–B.C.R.A. Isothermal calorimeter (*Figure 1*) a capacity of about 12 l. gives convenient dimensions, the water being concentrated around, with little below, the central space. Two $2\frac{1}{2}$ in. stirrers, in short convection tubes and

operating at *c.* 600 rev/min, give efficient stirring, the thrust bearings being mounted on the top of the jacket. A large capacity heater enables the approximate working temperature to be attained quickly and a heater of small capacity is then used for thermostatic control. It is convenient to sink the jacket into a bench or desk so that the operator can sit at his work; the insulation of the jacket by an air pocket decreases the energy consumption.

Calorimeter vessel

In the Griffin–B.C.R.A. Isothermal calorimeter the calorimeter vessel is of ovoid horizontal section, the stirrer operating in the narrow end. The vessel is made of Monel metal and has a handle which folds away clear of the vessel cover. It stands on three ebonite supports, which fit into indentations in the base; there is a 1 cm space below and around the vessel.

Covers

One of the essential features of the Griffin–B.C.R.A. Isothermal calorimeter is the double cover, which is fitted as one unit. It consists of two metallic covers, one to fit the calorimeter vessel and the other to rest on the jacket; these two covers are separated by a layer of blown-plastic insulator. Between the two covers there is also a collar which serves as a thermal break in the shaft of the stirrer for the calorimeter vessel; the stirrer is permanently fastened to the covers. The thin-wire electrical connection to the calorimeter bomb also passes through the cover and is connected, on the lower cover, to a spring contact which engages with the insulated terminal on the bomb when the covers are fixed. The other electrical connection to the bomb is made via the lower cover and the vessel with which this is in contact.

Operation

In accurate calorimetry, it is necessary to ensure that the bomb attains thermal equilibrium with its surroundings both before the sample is fired and before temperature readings cease to be taken. With an isothermal jacket heated to, say, 27°C and water added at 25°C and heated to a final temperature of 28°C, initial thermal equilibrium (i.e. before firing) would not quickly be attained if the bomb were cooled (in about 30 min) to air temperature between tests. To avoid excessive cooling between tests, the bomb should be emptied and stored in a thermostatically controlled cabinet (housing a tank containing the water used for charging the calorimeter vessel) or, alternatively, should be charged and returned to the empty calorimeter vessel. When no supply of heated water is available for the vessel, a heating coil may be used to raise the temperature to an appropriate level. When a supply is available, and when excessive cooling of the bomb has been avoided, thermal equilibrium is attained, using an efficient stirrer, within 5 or 10 min after the commencement of stirring (by an efficient stirrer). With a fore-period (for the evaluation of v') of 5 min, the vessel is therefore stirred for a total period of 10 to 15 min before firing the charge in the bomb.

After firing, a steady final rate of cooling (an average deviation of five successive 1-min values not exceeding 0·00072°C/min) should be attained in 6 or 7 min. Several determinations have been made in the Griffin–B.C.R.A. Isothermal calorimeter at different speeds of stirring (at least eight

XUM

tests at each speed), using benzoic acid (total heat release *c.* 7500 cal), with observations made for 20 min after firing. The results are recorded in *Table 3.* To eliminate the effect of the length of the chief period, the effective heat capacity was calculated for values of 6, 7, 8, 9, 10, 11 and 15 min in each test and the results averaged.

Table 3. Effect of speed of stirring in the Griffin–B.C.R.A. Isothermal calorimeter

Speed of stirring (rev/min)	136	210	245	360	440	550	600
Mean heat capacity (cal/°C)	2395	2391	2393	2392	2393	2394	2392
Standard deviation (cal/°C)	6·8	5·0	3·1	2·7	3·8	2·8	4·9
Mean average deviation of v″ (°C/min × 10⁴)	5·3	5·2	5·0	3·2	4·8	4·5	4·5

For speeds exceeding 136 rev/min, the values of the mean effective heat capacity are not significantly different. At 136 rev/min the mean is significantly different (95 per cent probability level) and the standard deviation is the highest of the series, so that it is concluded that a speed of stirring of 136 rev/min is too low. The average deviation of the final rate of cooling tends to fall with increase in the speed of stirring but the standard deviation, after falling to a low level for speeds of 245 to 550 rev/min, rises again at 600 rev/min. It was concluded that any speed within the 245 to 550 rev/min range should be suitable. The speed now used is 245 rev/min.

The results for speeds of 210 to 600 rev/min were then averaged for different lengths of chief period; these data are recorded in *Table 4.*

Table 4. Effect of length of chief period (speed of stirring 210 to 600 rev/min) in the Griffin–B.C.R.A. Isothermal calorimeter

Length of chief period (min)	7	8	9	10	11	15
Mean heat capacity (cal/°C)	2393·6	2392·4	2391·8	2391·7	2391·8	2392·9
Standard deviation (cal/°C)	3·6	3·8	3·5	3·9	4·4	4·7
Average deviation of v″ (°C/min × 10⁴)	3·0	4·8	4·9	4·2	4·7	4·5

It will be observed that the mean effective heat capacity is almost constant (2391·8) for chief periods of 9, 10 and 11 min, but that the values at 7 and 15 min are more than 1 cal/°C higher: this difference is significant (95 per cent probability level). It will be recalled that, in Part VII[1] of this series, it was pointed out that the observed effective heat capacity must be expected to vary with length of chief period, even given compliance with the rule suggested in Part III[2] for the selection of the point marking the end of the chief period. Further, the nature of the variation will depend upon the total heat release and the burning charactistics of the fuel. In the determination of effective heat capacity, the heat release should be substantially constant from test to test and only one material is involved, so that it seems desirable to define the length of the chief period as that which gives the best repeatability, i.e. any particular value from 7 to 10 min for a heat release of 7500 cal in the B.C.R.A. Isothermal calorimeter. A length of chief period of 7 min

has since been confirmed as that giving the lowest standard deviation in a series of 20 determinations using a platinum resistance thermometer and a Smith's Difference Bridge. With this refined method of temperature measurement, a standard deviation of 0·075 per cent was attained, i.e. half the practical lower limit when using mercury-in-glass thermometers.

Accepting that, in a determination of calorific value, the total heat release will, as advised[2], be approximately the same as in the determination of effective heat capacity, the value of the latter at a given time should depend only on the nature of the sample. Powdered coal is known to have roughly the same burning characteristics as briquetted benzoic acid, so that the correct length of chief period for a heat release of 7 500 cal from such a sample in the calorimeter under discussion is probably the same (7 min) as that defined for the determination of effective heat capacity. This, however, will not be true for cokes and liquid fuels, as the burning characteristics of these differ markedly from those of the standardizing substance. It is hoped that it will be possible to modify the burning characteristics of benzoic acid to comply with those of a variety of types of solid and liquid fuels; the calorimeter would then be calibrated for each type, the length of chief period used for evaluating the heat capacity, and subsequently applied rigorously in all determinations of calorific value of fuels of that type, being taken, in each case, as that giving the best repeatability. It should be emphasized that, in routine fuel calorimetry, the rule advised in Part III[2] of this series is still recommended as the method of selection of the point marking the end of the chief period. The Griffin–B.C.R.A. Isothermal calorimeter has been found to be an excellent calorimeter for routine fuel analysis, but, in addition (and particularly in conjunction with the refined method of temperature measurement mentioned above), it is capable of use in calorimetric studies requiring a high degree of accuracy: it is in such studies that the detailed consideration of the effect of length of chief period is necessary.

ADIABATIC SYSTEMS

One of the earliest adiabatic calorimeters was that used by T. W. RICHARDS, L. J. HENDERSON and H. L. FREVERT[12] in their work on the heating value of hydrocarbons. A silver calorimeter vessel contained the bomb and 4·4 l. of water, which was stirred with a reciprocating stirrer. The jacket, from which the vessel was separated at the sides and bottom by an air space of 0·5 cm, contained alkali, which was stirred. Over the whole of the open jacket and calorimeter vessel, a short cylinder with an open top was placed. This had tubes for the stirrer shafts and thermometer and the alkali in it was also stirred by the reciprocating stirrer. During a determination, acid was added from burette to the main and subsidiary jackets, the aim being that the heat of reaction should keep the jacket at the same temperature as the calorimeter vessel.

T. W. RICHARDS and R. H. JESSE[13] improved the design, this version being illustrated in *Figure 2*. In this, the separate jackets were combined and a single calorimeter vessel lid was clipped on, a rubber jacket making it watertight. The temperature in the jacket could readily be kept within $\pm 0{\cdot}1\,^{\circ}C$ of that of the calorimeter vessel. This system is not suitable for routine calorimetry.

XUM

F. G. BENEDICT and H. L. HIGGINS[14] used an adiabatic calorimeter in which the temperature in the outer jacket was adjusted by means of an electrical heater and a supply of cold water, the excess overflowing round the outer cylinder of the jacket and the jacket and calorimeter vessel being covered with two dead-air compartments.

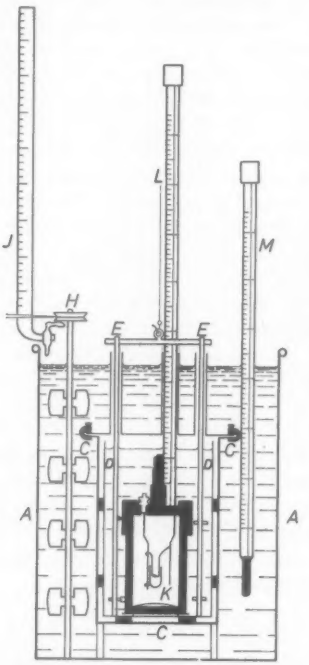

Figure 2. Richards Adiabatic calorimeter showing: A outer vessel, C nickel-plated copper can, D silver calorimeter vessel, E stirrer for calorimeter vessel, H stirrer for jacket, J burette, K crucible, L thermometer for calorimeter, M thermometer for jacket

Perhaps the best known adiabatic calorimeter is that devised by S. W. PARR[15]. This has a calorimeter vessel of oval-shaped horizontal section and a stirrer shaft at one end. The jacket has an elliptical (horizontal section) inner and a square (do) outer vessel, the latter being surrounded by an air space and contained in a cubical wooden box. Water is circulated in this jacket and through a compartment in a lid from which it overflows to an outlet; as the lid is lifted, the compartment effectively empties. A horizontal rotary stirrer in the bottom of the jacket lifts the water through a convection tube to the lid, this stirrer and that in the calorimeter vessel being operated at 800 rev/min by a motor mounted on a baseplate outside the jacket cabinet. Hot and cold water are supplied to the jacket, the adjustment of the two rates of flow enabling the temperature in the jacket to be maintained (ideally) equal to that of the calorimeter vessel. In the model used by the writer, the hot water was supplied by an instantaneous gas heater and cold water was obtained from the mains; each supply led first to an overflow vessel, from which the flow to the jacket was controlled by a screw clip on a rubber

connection. (Electrical heating can be used, and is preferable in a small laboratory where the aldehydes from the instantaneous gas heater can be offensive.) Two bomb-calorimeter thermometers are used, one in the calorimeter vessel and one in the jacket; between tests, the thermometers are raised and the lid swung to one side, this operation being impossible until the thermometers are safely out of the way. The Parr calorimeter is illustrated in *Figure 3.*

Work has now been in progress for some years on the development of a new adiabatic calorimeter. In the first prototype of this, the B.C.R.A.

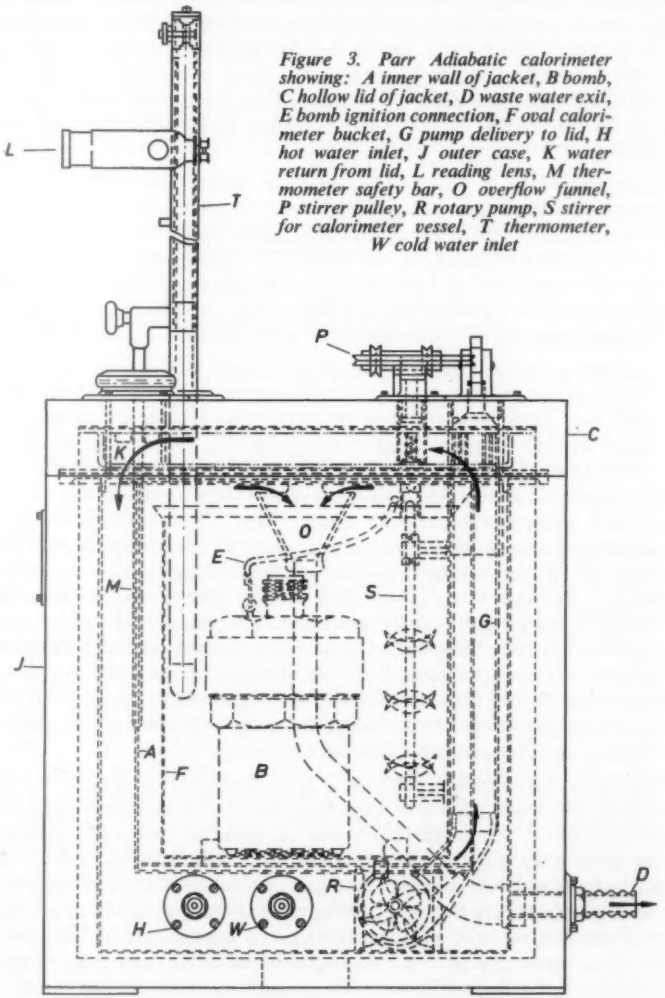

Figure 3. Parr Adiabatic calorimeter showing: A inner wall of jacket, B bomb, C hollow lid of jacket, D waste water exit, E bomb ignition connection, F oval calorimeter bucket, G pump delivery to lid, H hot water inlet, J outer case, K water return from lid, L reading lens, M thermometer safety bar, O overflow funnel, P stirrer pulley, R rotary pump, S stirrer for calorimeter vessel, T thermometer, W cold water inlet

XUM

Adiabatic calorimeter, a turbine stirrer and convection jacket, as recommended by J. COOPS and K. VAN NES[16], were used, the aim being to promote efficient circulation of water in the cylindrical calorimeter vessel and washing of the lower surface of the lid, so that, with suitable insulation above, there would be no need for a circulation of jacket water above the lid. The cover of the calorimeter vessel fitted outside the vessel and approximately 1 cm outside this there was a second cover which fitted on the water side of the inner shell of the annular jacket. These two metal covers were secured to a wooden lid (with a dead-air space) which also covered the open water-jacket. Suspended from the two metal covers was a metal plate resting loosely on the top of the cylindrical convection jacket, which had a hole in its base. The turbine pump, secured to the lid, rotated in the space above the convection jacket cover and the cover of the calorimeter vessel, drawing water through a hole in the centre of the convection cover: the water entered the hole in the base of the convection jacket and returned outside this jacket.

One disadvantage of this system was that water was flung through the covers and entered the air space. This was overcome in the next prototype by discarding the cover of the convection jacket, and extending the walls of this so that it reached nearly to the cover of the calorimeter vessel. The top portion was castellated to break the force of the water thrown out by the pump and to allow the water to overflow. Also, the flange on the cover on the calorimeter vessel was altered to fit inside instead of outside the vessel.

In the first prototype, which was of the 'overflow' type, an attempt was made to match the jacket and vessel temperatures by means of thermistors balanced on a Wheatstone bridge, the water being heated by means of an immersion heater. Due to a lag in response, this was not satisfactory, so that, in the next prototype, the overflow system was abandoned. The design of the jacket was altered to allow for the use of a constant flow of water, instead of a variable amount with an overflow. This was achieved by providing separate means for heating and cooling of water flowing to, through and from the jacket in closed circuit. In the new design, water was withdrawn from the base of the jacket by a turbine pump, passed to the heater and returned (tangentially) to 2 positions near the top of the water surface. The heater consisted of a spiral of nickel–chromium tubing in a Perspex box through which the water passed; it was designed to raise the whole of the water through the (approximately) 3°C rise expected to occur in the vessel during a determination. For cooling between tests, the nickel–chromium spiral tube was supplied with cold water.

A series of tests has been carried out to compare the B.C.R.A. (second prototype) and Parr Adiabatic calorimeters. To determine whether, with adiabatic control, the repeatability was as good as that with an ordinary system using a static jacket, each system was tested both with the water in the jacket static and with the temperature of this water adiabatically controlled. The heat supply to the B.C.R.A. Calorimeter was controlled with a Variac. In each test, benzoic acid was burned to give a heat release of 7 500 cal. The results are summarized in *Table 5.* It should be noted here that, in general, owing to small but finite differences in temperature between jacket and vessel

during the course of a determination, a cooling correction must still be applied to an 'adiabatic' calorimeter if an accurate result is required. The correction may be shown to be given by the equation

$$C = n(w - s) + K[\sum_{1}^{n-1}(\delta t_x) + \tfrac{1}{2}(\delta t_0 + \delta t_n)]^{\circ}C \qquad \ldots . [2]$$

where n = length of chief period (min), w = rate of fall of temperature due to evaporation (°C/min), s = rate of rise of temperature due to stirring (°C/min), $\delta t = t_c - t_j$ (°C), and x = time (min) measured during chief period (0 to n min). The calorimeter constant (K) can be found from a series of tests using the calorimeter as a static system. From the same series, $(w - s)$ may be estimated by putting

$$w - s = v - K\overline{\delta t} \qquad \ldots . [3]$$

where $\overline{\delta t}$ = mean temperature difference during a steady state (fore- or after-period) (°C). In *Table 5*, the data given for adiabatic tests have all been so corrected.

Table 5. Results of determinations of effective heat capacities of B.C.R.A. and Parr adiabatic systems used with static and adiabatic jackets

System	Jacket control	No. of tests	Mean heat capacity (cal/°C)	σ* %	Mean n min	$\delta t = (t_c - t_j)$ °C				
						Mean δt_0	Mean δt_n	Mean†	Max.†	Min.†
B.C.R.A.	*Static*	7	2040	0·16	6·1	—	—	—	—	—
	Adiabatic	10	2040	0·13	7	0·06	−0·02	0·10	0·19	−0·08
Parr	*Static*	9	2428	0·24	7·9	—	—	—	—	—
	Adiabatic	16	2428	0·26	10	0·02	−0·02	0·00	0·10	0·01

* σ = standard deviation. † For all values of x.

It will be observed that the manually controlled Parr system gives excellent matching between jacket and calorimeter temperatures. Nevertheless, without the application of the cooling correction (equation 2) the mean observed effective heat capacity was significantly higher (2436 cal/°C) than when using the system as a static one. A similar difference was noted for the B.C.R.A. system, but, having applied the correction, the mean values were found to agree in both cases. T. W. RICHARDS and L. L. BURGESS[17] advised that the maximum temperature difference be 0·1°C; it has now been established that, even when this is complied with, a cooling correction is strictly necessary. However, in routine calorimetry the correction could be ignored provided the heat release and length of chief period were the same as in the determination of the effective heat capacity, the correction being then also ignored.

The data of *Table 5* show that the B.C.R.A. system gives better repeatability than does the Parr calorimeter. This must be ascribed to the two main improvements of the B.C.R.A. design over Parr's: the use of a lid which practically eliminates loss by evaporation and the use of a better water-circulation system; further, it seems that the circulation of water above the

XUM

lid in the Parr system is less effective than the circulation below the lid in the B.C.R.A. system.

In another series of ten tests with the B.C.R.A. system, designed to see if the time of stirring before firing could be reduced from five to two minutes (a 5 min fore-period being no longer required for the cooling correction), the standard deviation was 0·33 per cent, showing that stirring for at least 5 min before firing is desirable to obtain an accurate value of the temperature on firing. In another series of eighteen adiabatic tests with the B.C.R.A. Adiabatic calorimeter, the repeatability was assessed for different limiting values of the mean value of $(t_c - t_j)$: for $(t_c - t_j)$ not greater than 0·20, 0·10 and 0·05°C, respectively, the standard deviation in 18, 12, and 9 tests was 0·20 per cent in each case. There is, therefore, no gain in repeatability due to a reduction of $(t_c - t_j)$ over the range specified.

As previously indicated, in accurate non-adiabatic calorimetry, the length of chief period should be fixed (and steps taken to ensure that, at the fixed point, the effective heat capacity is the same in a determination of calorific value as in the standardization of the calorimeter). In routine calorimetry, a fixed length is a convenience, but, with a non-adiabatic system, the length must be chosen so as to ensure compliance with the rule laid down in Part III[2] of this series. In adiabatic calorimetry, a fixed length is not only a convenience but also a necessity if the cooling correction is to be ignored. Given agreement of the corrected effective heat capacity with that obtaining under static conditions, the choice of length of chief period may be made so as to ensure the best repeatability. For the B.C.R.A. Adiabatic calorimeter, calculation of the mean effective heat capacities and standard deviations for lengths of chief period of 6, 7 . . . 12 min in the 10 adiabatic tests of *Table 5* shows that neither the mean nor the standard deviation changes significantly over the period specified. Any length between 6 and 12 min could therefore be chosen for the chief period, the actual value being a matter of convenience: 6 min to give minimum time of test or 10 min for a round number.

The latest development of the B.C.R.A. Adiabatic calorimeter has been concerned with the introduction of effective automatic control; this has now been achieved by the application of an electronic control system to the thermistor arrangement of the first prototype. Equality of temperature in jacket and vessel gives balance in a thermistor bridge. (The jacket thermistor is actually in the Perspex box.) Any out-of-balance e.m.f. is amplified, passed through a phase detector to determine the sense of the out-of-balance, and used to control the heating arrangements. If the heat requirements are too great for the main heater (a carbon rod in the Perspex box), an auxiliary heater (the nickel–chromium spiral) is switched into the circuit and if the signal indicates that heat should be extracted from the system, a cooling-water flow (through the spiral of nickel–chromium tubing) is switched in. Provision is made for switching in an auxiliary resistance in the bridge to allow control of the calorimeter whilst the vessel thermistor is out of the water. The arrangement is illustrated diagrammatically in *Figure 4*.

The electronic control system enables the temperature in the jacket of the B.C.R.A. Adiabatic calorimeter to be maintained within 0·1°C of that in the calorimeter vessel at all times during a determination. When using this

system, the standard deviation of single determinations of effective heat capacity is of the same order as that reported for tests using manual control (0·15 to 0·20 per cent). With either system of control, this calorimeter is, therefore, capable of better repeatability than is the best known commercially available (Parr) adiabatic calorimeter. With the electronic control system,

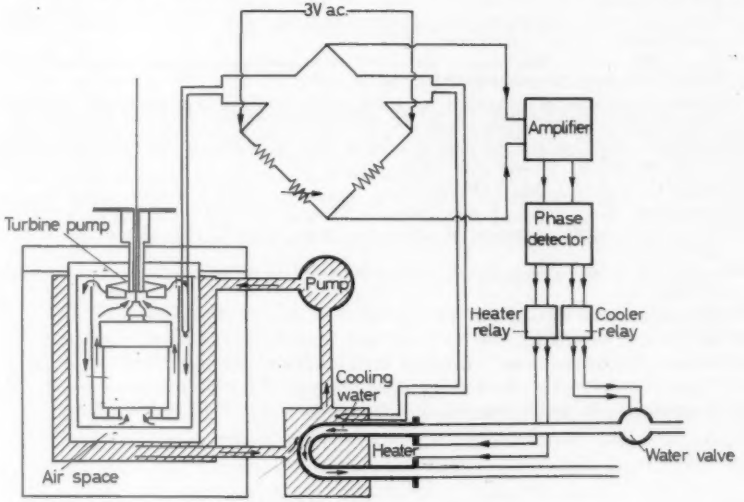

Figure 4. B.C.R.A. Adiabatic calorimeter (schematic)

it is also much simpler to use and, therefore, more appropriate to the conditions under which an adiabatic calorimeter is normally used. As no cooling correction is necessary (under the conditions specified), no fore- and after-periods are required. There is thus a saving of time in respect of both experiment and calculation. As the actual test occupies some 11 to 15 min (5 min stirring period plus chief period of 6 to 10 min), it will be appreciated that a single determination can be completed in about 20 min. Thus a single operator can make 18 or 20 determinations in a working day. An adiabatic system is therefore particularly suitable where a very large number of determinations are required per day. The B.C.R.A. Adiabatic calorimeter enables a high rate of working to be maintained with little or no loss in accuracy and without undue strain on the operator.

Several members of the staff of the Midland Coke Research Station have been concerned in the work reported here. The work formed part of the programme of the British Coke Research Association, to whom the author is indebted for permission to publish.

British Coke Research Association,
74 Grosvenor Street,
London, W.1.

(*Received February 1957*)

REFERENCES

[1] MOTT, R. A. *Fuel, Lond.* 36 (1957) 447

[2] BARKER, J. E., MOTT, R. A. and THOMAS, W. C. *Fuel. Lond.* 34 (1955) 283

[3] *Phys. chem. Surv. Nat. Coal Resour. No. 7*, p 12. Her Majesty's Stationery Office: London, 1927

[4] *Phys. chem. Surv. Nat. Coal Resour. No. 44*, p 44. Her Majesty's Stationery Office: London, 1940

[5] 'Methods for the analysis and testing of coal and coke' *B.S. 1016: 1942*, p 55. British Standards Institution: London

[6] 'Feste Brennstoffe: Bestimmung der Verbrennungswärme und des Heizwertes' *DIN 51708*. Deutscher Normenausschuss: Berlin, 1950

[7] 'Standard methods of laboratory sampling and analysis of coal and coke' *D271–48*. American Society for Testing Materials: Philadelphia, 1948

[8] 'Standard method of test for thermal value of fuel oil' *D240–39*. American Society for Testing Materials: Philadelphia, 1939

[9] MOTT, R. A. *Fuel. Lond.* 35 (1956) 261

[10] DICKINSON, H. C. *Bull. U.S. Bur. Stand.* 11 (1914) 189; S 230

[11] CHALLONER, A. R., GUNDRY, H. A. and MEETHAM, A. R. *Phil. Trans.* Ser. A, 247 (1955) 553

[12] RICHARDS, T. W., HENDERSON, L. J. and FREVERT, H. L. *Proc. Amer. Acad. Arts Sci.* 42 (1907) 573

[13] RICHARDS, T. W. and JESSE, R. H. *J. Amer. chem. Soc.* 32 (1910) 269

[14] BENEDICT, F. G. and HIGGINS, H. L. *J. Amer. chem. Soc.* 32 (1910) 461

[15] PARR, S. W. *8th int. Congr. Chem.* Vol. I, p 389. Washington and New York, 1912

[16] COOPS, J. and VAN NES, K. *Rec. Trav. chim. Pays-Bas* 66 (1947) 131

[17] RICHARDS, T. W. and BURGESS, L. L. *J. Amer. chem. Soc.* 32 (1910) 431

Rates of Reaction in the Carbonization Process

G. R. OXLEY and G. J. PITT

An apparatus has been constructed in which coal can be carbonized isothermally, and has been used to study the formation of chloroform-soluble material during carbonization. The results show that the rate of formation of the chloroform-soluble material is much higher than the rate of development of fluidity in the coal. It is concluded that the chloroform-soluble extract cannot be identified with the 'fluid coal' postulated by Fitzgerald as the intermediate pyrolysis product responsible for fluidity, since some factor, other than extract yield, must play an important part in determining the kinetics of fluidity.

THE solubility of a coking coal in solvents such as pyridine and chloroform increases appreciably if the coal is heated to about 400°C and cooled before extraction. Moreover the residue after extraction is non-swelling, whereas the extract when mixed with a non-coking coal will cause it to swell and form a coherent coke[1]. The reactions associated with the changing solubility are evidently of importance in the process of carbonization, and it has been suggested that the material extracted by chloroform after preheating the coal is associated with the plastic behaviour of the coal.

The changes in fluidity of a coking coal when heated in the plastic range have been considered by previous workers to be consistent, in general terms, with decomposition reactions occurring during this stage of pyrolysis[2]. Fitzgerald has developed a quantitative theory which accounts for these changes on the assumption of two consecutive first-order reactions, the intermediate product, 'fluid coal', being responsible for fluidity. Values for the velocity constants and energies of activation of the reactions were obtained[3]. The object of the present work was to investigate the kinetics of the formation of the chloroform-soluble extract in order to obtain parameters for comparison with those derived by Fitzgerald's method, and thus to determine whether the chloroform-soluble extract is responsible for the development of fluidity.

Previous workers have been principally interested in the variation of yield with preheating temperature, and the experimental conditions have not been designed for the study of the effect of varying times of heating at a particular temperature. I. G. C. DRYDEN and K. S. PANKHURST[1] have published one graph showing the yield of extract as a function of carbonizing time at 420°C, but in their apparatus the time for the coal to attain this temperature was about 30 minutes, and consequently their results are subject to uncertainty in this initial period. In the present work an apparatus has been constructed in which coal can be carbonized for measured periods of time under substantially isothermal conditions.

XUM

EXPERIMENTAL

The apparatus is based on a design by H. N. STONE *et al.*[4], which was used in the study of the rates of devolatilization of coals. In their apparatus, the coal was injected into a fluidized bed of sand in the reactor, and the heat required to raise the temperature of the coal came from the sand. In this way the coal was heated very rapidly, but the temperature of the sand–coal mixture was lower than that of the walls of the reactor, and about five minutes elapsed before equalization was complete. This difficulty has been largely overcome in our apparatus by preheating the sand in a separate fluidized heater to such a temperature that when the sand and coal are mixed in passage into the reactor, the resultant temperature of the mixture is equal to that of the walls of the reactor. Minor temperature differences are sometimes observed but temperature equilibrium is achieved in less than 15 seconds. Samples of the sand–coal mixture are withdrawn from the reactor at selected times by opening a cock on a side tube connected to an evacuated and cooled metal receiver. The temperature of the coal is thus reduced below 100°C in less than 5 seconds.

Experiments have so far been carried out with one coking coal (Union Hill Top Drift, V.M. 30·3 per cent d.a.f., C.R.C. 401). The 30 to 60 B.S.S. size range fluidizes satisfactorily with 52 to 72 B.S.S. sand (as used for A.V. tests), and the risk of coking in the reactor is very small if the ratio of sand to coal exceeds the agglutinating value. The use of a high ratio has the additional advantage that the initial sand temperature required is but little higher than that of the reactor. The weight of the coal sample is about 33 g and that of the sand about 970 g. The bed is fluidized with ten litres nitrogen per minute. No attempt has been made to separate the sand from the carbonized coal in the samples from the reactor. The extraction with chloroform is performed on portions of the mixture in a Soxhlet extractor for four days. After extraction, the residue is dried at 110°C, ashed at 775°C and weighed to determine the weight of carbonized coal initially in the mixture. The weight of extract can thus be expressed as a percentage of the weight of char. The volatile content of another portion of the unextracted mixture is determined, using a modified type of crucible and an amount of sample such that the weight of char and the thickness of the layer in the crucible correspond fairly closely with those in the standard test. Assuming that 'fixed carbon' is unaffected in the carbonization, the yield of extract may thus be expressed as a percentage of the original coal.

Gieseler measurements at constant temperatures were also carried out on the same batch of coal, using an apparatus similar to that described by D. FITZGERALD[3]. Whereas in Fitzgerald's experiments the coal was placed in the apparatus at 300°C and heated to the required temperature at 3°C/min, in the present tests the apparatus was brought to the required temperature before the coal was inserted; about eleven minutes elapsed before the coal attained a constant temperature. The variation of the fluidity with time (measured from the instant when the coal was placed in the hot vessel) was measured at a series of temperatures from 400° to 440°C. At temperatures below 400°C the fluidity is too small to measure.

RESULTS AND DISCUSSION

Figures 1 and *2* show the variation of the yield of chloroform-soluble material with time for the coal carbonized at temperatures from 290° to 450°C. The point plotted for zero time corresponds to the percentage extract from the uncarbonized coal. The curve for 290°C shows that the amount of extract formed at that temperature is small. The initial portions of the curves for

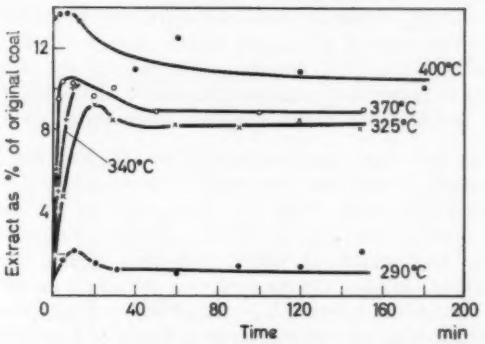

Figure 1. Yield of extract as a function of time of carbonization

higher temperatures rise steeply, the slope increasing with temperature until, at 400°C the rising portion is practically complete in five seconds and cannot be plotted by this method. The rising portions of the curves for 325°, 340° and 370°C are consistent with the assumption that the extract is a product of a first-order reaction with apparent activation energy about 30 kcal/mole and frequency factor 4×10^{10} min^{-1}.

The later portions of the curves, particularly that for 340°C, are known with less certainty, and form the subject of further investigation. After

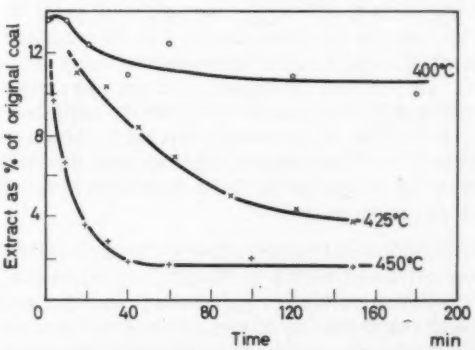

Figure 2. Yield of extract as a function of time of carbonization

passing through shallow maxima, the amounts of extract at temperatures up to 400°C become constant, indicating that the extracts are stable for times up to three hours. The shallow maxima may arise from the extraction of that portion of the volatile matter which would have been liberated at that temperature but which was held in the pores of the sample when quenched.

XUM

The curve for 400°C appears to indicate a transition from the type described above to that characteristic of higher temperatures. At 425° and 450°C the amount of extract increases extremely rapidly at first and then decreases again. If the extract is a product of a first-order reaction, it would appear that this material undergoes a further reaction at these temperatures which renders it insoluble again. A system of reactions of this type was postulated by Dryden and Pankhurst to explain the form of curve obtained in their experiment. However, it will be noted that the results reported here do not show the amount of extract falling asymptotically to zero with increasing time, as would be expected on the basis of the simple theory of two consecutive first-order reactions[3]. At 450°C the limiting value is about 1·8 per cent and at 425°C it would appear to be about 3·3 per cent.

This behaviour may be explained by assuming that the extractable material is complex, and that the different components decompose with differing velocity constants. Thus one component of the material may decompose and become insoluble at 425°C, whereas another component may remain stable and soluble at 450°C and even higher temperatures. (A similar phenomenon occurs in the evolution of volatile matter during carbonization.) An alternative hypothesis is that two simultaneous reactions occur in the decomposition of the extractable material, the product of one reaction being soluble in chloroform and that of the other being insoluble. If the activation energy of the first reaction was lower than that of the second, an increase in temperature would favour the formation of the insoluble product, and the observed decrease in the limiting solubility with increasing temperature could be explained. From the extract yield/time curves it is not possible to distinguish between these hypotheses without a knowledge of molecular weights of the extracts. It might be thought, *a priori*, that the former hypothesis is more likely, but there is some evidence which favours the latter. The extracts obtained from the coal heated at 450°C for 1 to 3 hours are pitch-like with a sufficiently low softening point to flow slowly at 100°C, whereas extracts corresponding to 5 to 10 minutes heating are brittle, flaky solids which do not exhibit appreciable fluidity at temperatures below about 250°C. On the first hypothesis, the pitch-like material must be present in the brittle solid, and would therefore be expected to confer some fluidity on it. According to the second hypothesis, however, the pitch-like material would be the soluble product resulting from the simultaneous decomposition reactions which the brittle solid undergoes; this appears to be the more reasonable assumption.

The experimental curves relating the fluidity of the coal to the time of carbonization are shown in *Figure 3*. Comparison of these fluidity curves with the extract curves in *Figure 2* shows first that at any temperature between 400° and 440°C the rate of formation of the extract is much greater than the rate of development of fluidity. At 400°C, for instance, the maximum yield of extract is obtained almost at once, whereas about one hour elapses before the fluidity reaches a maximum. The difference is large enough to outweigh the differences in the conditions in the two sets of experiments. Secondly, it will be noted that solubility in chloroform remains appreciable at 425°C for times greater than two hours, whereas the fluidity has then become too

small to measure. It is therefore concluded that the extract cannot be identified with Fitzgerald's 'fluid coal', since there is clearly some other factor which has an overriding influence in determining the rates of development and decay of fluidity.

Dryden and Pankhurst, in their discussion of the relation between the chloroform extract and the fluid properties of the coal, suggested that a certain minimum concentration of extract might be necessary before the coal

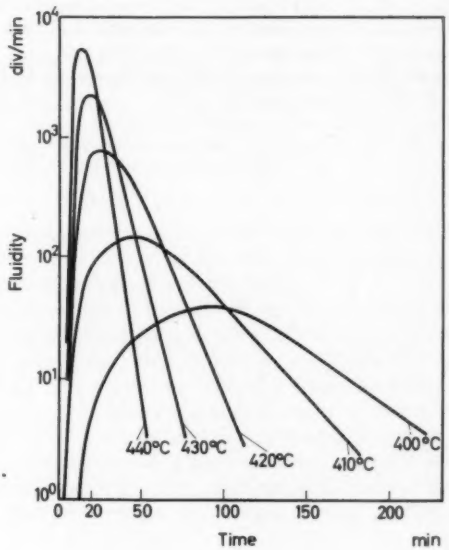

Figure 3. Fluidity of Union coal as a function of carbonizing time

exhibits fluidity. This suggestion is at variance with the present experimental facts. Thus there is about 9 per cent yield of extract but no fluidity in the coal heated at 370°C, whilst there is less than 8 per cent yield of extract and appreciable fluidity in the coal which has been heated at 425°C for about one hour.

The role of the chloroform-soluble material in the process of carbonization therefore remains unexplained. Some elucidation may follow from a more detailed study of the changes in the properties of the extracts with time at temperatures over 400°C, and from an investigation of the effect on fluidity of removing the extract formed at temperatures below the plastic range. This work is being continued.

The constant temperature Gieseler experiments were performed by Dr R. G. Partington. The work described in this paper was carried out as part of the research programme of the Scientific Department of the National Coal

XUM

Board. The views expressed are those of the authors and not necessarily those of the Board.

National Coal Board,
Coal Research Establishment,
Stoke Orchard,
Cheltenham, Glos.

(*Received March 1957*)

REFERENCES

[1] DRYDEN, I. G. C. and PANKHURST, K. S. *Fuel, Lond.* 34 (1955) 363
[2] DRYDEN, I. G. C. and GRIFFITH, M. *Mon. Bull. Brit. Coal Util. Res. Ass.* 18 (1954) 62
[3] FITZGERALD, D. *Trans. Faraday Soc.* 52 (1956) 362
[4] STONE, H. N., BATCHELOR, J. D. and JOHNSTONE, H. F. *Industr. Engng Chem. (Industr.)* 46 (1954) 274

The Interaction of Organic Vapours with Coal I—The Reversible Sorption of Methanol and Pentane

P. FUGASSI, R. HUDSON and G. OSTAPCHENKO

The sorption of methanol and n-pentane on Pittsburgh seam coal has been investigated at 35°C using a gravimetric method. The sorption is isothermally reversible. The sorption and desorption of methanol on a given coal sample increases the subsequent sorption of pentane by about 100 per cent. Pentane sorption and desorption decreases the subsequent sorption of methanol by about 10 per cent. These data indicate that the structure of the coal gel is changed irreversibly by the sorption of methanol and pentane.

COAL is a porous gel but the details of its pore structure are still in dispute. Measurements of the surface area of coal by the BET method using nitrogen and argon give much smaller internal areas (by a factor of 10 or more) than those obtained by the determination of the heat of wetting of coal by methanol. A recent model[1] for the structure of coal ascribes two types of internal surface area to coal. The first type is that caused by a wide distribution of large pores and accounts for about one per cent of the total surface area as determined by heat of wetting and the second type is due to a system of very fine pores (approximately 10Å in radius) and is responsible for most of the internal surface area. The correlation of a coal structure with the sorption data on coal for polar and non-polar gases is still in dispute. A recent publication by R. B. ANDERSON and co-workers[2] reviews the current aspects of the problem.

It is the purpose of this communication to describe the sorption of methanol and *n*-pentane on coal carried out gravimetrically at 35°C.

EXPERIMENTAL

Chemicals

The work described herein was confined to Pittsburgh seam (Edenborn) coal. The material is stored in the form of ¼-in. pieces and is the same sample used by R. A. GLENN[3] who gives proximate and ultimate analyses for the material. It was ground by passage through a hammer mill. The sample as used was unsieved. It contained particles which range from −60 to −300 mesh. *n*-Pentane was a Matheson product; it was distilled before use. Absolute methanol, A.R., a Mallinckrodt product was used as received. In some cases, the methanol was stored over a drying agent, but no differences were noted.

Apparatus

A McBain–Bakr adsorption apparatus was used. The spring was constructed from Ni-Span C wire[4], 0·005 in. in diameter, The spring was calibrated for loads up to 1·5 g and to that point its response was linear, having a sensitivity

XUM

of 0·0042 g/mm. The coal sample is carried in a glass bucket hung on the end of the spring. The bucket weight is around 0·15 g and the coal samples used were around 0·5 g. With a cathetometer reading to 0·1 mm a precision of better than 0·1 per cent could be obtained. The remainder of the apparatus consisted of manometer, two storage reservoirs for methanol and pentane, and the vacuum system. Short form mercury cut-offs were used throughout[5]. The pumping system consisted of a two-stage mercury diffusion pump backed by the usual mechanical pump. The entire apparatus was enclosed in an air thermostat held to 35·0°C ± 0·10.

Procedure

The sample of coal was weighed, placed in the apparatus and allowed to stand for one hour at 35°C with air in the apparatus. The elongation of the spring was then measured using a cathetometer. It was assumed that during this initial period the sample did not lose appreciable amounts of water or adsorb appreciable amounts of mercury vapour. The system was then evacuated for eight hours and the sample allowed to stand for an additional sixteen hours under high vacuum. Usually no change in weight resulted during the sixteen-hour period. The loss of weight of the sample for air-dried coal was around 1·5 per cent. By drying the sample at 35°C in a desiccator for varying periods of time, the loss in weight could be reduced to 0·4 per cent. In all cases the sample lost weight. Since during the initial waiting period it can be assumed that the adsorption of mercury vapour is very small, these results show that the adsorption of mercury vapour, which is always present at a relative pressure of 1, is either very small or very slow. After initial evacuation the desired vapour was admitted to the apparatus at a known pressure and the system was allowed to stand for 24 hours so that the coal sample came to equilibrium. The running of an isotherm with six experimental points hence involved a period of one week. No correction for changing buoyancy as the pressure of vapour changed was applied. Even at the highest pressures used, the buoyancy correction only amounted to about 0·1 per cent of the total weight. Separate experiments with empty buckets showed that the adsorption of the vapours on the glass surface could be ignored at relative pressures of 0·8 or lower.

EXPERIMENTAL RESULTS

Sorption experiments

In *Figure 1*, the sorption isotherm part of the complete cycle (sorption followed by desorption) is shown. For methanol the experimental points on the desorption isotherm portion of the cycle lie above the sorption isotherm points and have not been plotted. Such a hysteresis loop is not uncommon. In *Figure 1*, the top curve represents the initial sorption of methanol on the coal. Following desorption of the methanol to constant (initial) weight the sorption isotherm for pentane was measured and is shown by the lowest curve. After desorption of pentane, the methanol isotherm was repeated and is shown by the middle curve in *Figure 1*.

Similar sequences, using, in turn, pentane, methanol, pentane have been run but have not been illustrated. The initial sorption of pentane on coal gives an isotherm similar to the one shown in *Figure 1*, except that from

relative pressures of 0·2 to 0·7, the sorption varies from 1×10^{-4} to 2×10^{-4} moles of pentane per gramme of coal. Reference to the lowest graph on *Figure 1* shows that the analogous value of pentane adsorption subsequent to methanol treatment, for the same range of relative pressure, varies from $3{\cdot}7 \times 10^{-4}$ to $4{\cdot}1 \times 10^{-4}$. In other words, sorption of methanol increases the subsequent sorption of pentane while sorption of pentane decreases the subsequent sorption of methanol.

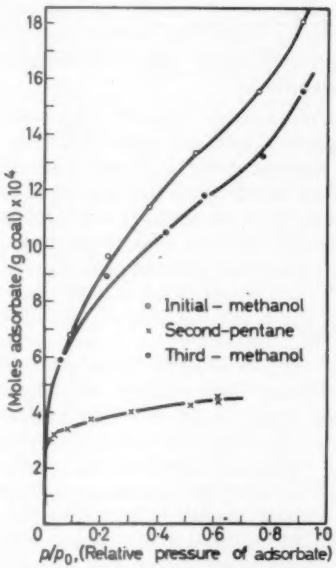

Figure 1. Sorption of methanol and pentane on coal

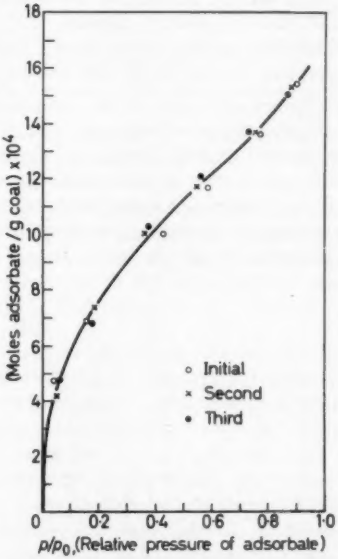

Figure 2. Sorption of methanol on pentane extracted coal

Figure 2 represents sorption isotherm points obtained by running three complete cycles of sorption and desorption using in each case methanol vapour. The experimental points for the desorption portion of the cycle lie above the points for the sorption portion of the cycle and have not been plotted in *Figure 2*. The sorption points all fall along the same line, indicating that the gel structure of the coal has changed to some equilibrium configuration with respect to time of exposure, as some points on the initial cycle represent exposure for periods of time of about two days, while other points on the third cycle represent exposure for periods of time of some twenty days. The data in *Figure 3* were obtained using a coal sample extracted with liquid pentane for several weeks. Comparison of the isotherm in *Figure 2* with the middle isotherm shown in *Figure 1* shows the close agreement of the two curves. Extraction of the coal with pentane apparently causes the same change in gel structure as that caused by sorption of pentane vapour.

Extraction experiments

In connection with the above results, it will be of interest to discuss a few

preliminary results of the extraction experiments being done in this laboratory. Extractions with methanol and pentane were carried out in the conventional Soxhlet apparatus at atmospheric pressure. In some cases, the contents of the apparatus were protected against atmospheric moisture; in all cases air was present. Both methanol and pentane are known to be poor solvents for coal; the amount of extract obtained in each case is small.

With pentane, after extraction for about 100 hours, the amount of extract obtained was 0·2 per cent of the original weight of the coal. 80 per cent of the extract was elemental sulphur, identified by crystalline habits, transition temperature, melting point and a number of chemical tests. The remaining 20 per cent of the extract has not been identified.

Methanol extraction was carried out for one month. About 0·80 per cent of the original weight of the coal was extracted. A qualitative analysis showed that the extract contained iron, a small amount of sulphur, and a trace of aluminium. About 20 per cent of the extract was iron. As the sample of coal being used contained about 0·4 per cent iron, the methanol has removed about 40 per cent of the iron originally present in the coal. The organic constituents associated with the iron are probably a mixture and have not been identified as yet.

DISCUSSION

From their known chemical properties, it would be anticipated that methanol and *n*-pentane are inert at 35°C with respect to coal. A check on this conclusion is obtained by comparing the initial weight of the coal sample against its weight after a completed cycle of sorption and desorption of a given vapour. For experiments using alcohol alone, the average change in weight is about 0·30 per cent. Experiments with pentane or experiments using a sequence involving pentane and alcohol show an average change in weight of about 1·2 per cent. In either case, it is considered that the reaction of coal with either solvent is negligible and that the sorption of pentane and methanol on coal is reversible.

The data show that the sorption of pentane or methanol changes the gel structure of coal irreversibly. The gel structure of a given coal sample then is a function of the history of that coal sample. One might suspect from these experiments that the sorption at the higher relative pressures of a condensible vapour of any type, where such a vapour can permeate the pore structure, will always lead to a change in the gel structure.

Coal Research Laboratory,
Department of Chemistry,
Carnegie Institute of Technology,
Pittsburgh 13, Pennsylvania

(*Received February 1957*)

REFERENCES

[1] ZWIETERING, P. and VAN KREVELEN, D. W. *Fuel, Lond.* 33 (1954) 331
[2] ANDERSON, R. B., HALL, W. K., LECKY, J. A. and STEIN, K. C. *J. phys. Chem.* 60 (1956) 1548
[3] GLENN, R. A. *Fuel, Lond.* 34 (1955) 202
[4] MUDGE, W. A. and TALBOT, A. M. *Iron Age* 157 (25 Apr 1946) 66
[5] WARRICK, E. and FUGASSI, P. *Industr. Engng Chem. (Anal.)* 15 (1943) 13

The Nature of Reactive Groups in Abnormal Coals

M. S. IYENGAR and A. LAHIRI

In abnormal coals high swelling number tends to be associated with low oxygenated reactive groups and low heats of wetting in methanol.

IT IS well known that some coals of very high organic sulphur content, such as are found in certain parts of India, Australia, Pakistan, Borneo and Europe, exhibit the dual characteristics of low and high rank coals. Most of these coals exhibit coking properties and have generally exceedingly low softening point and high maximum fluidity, but with these properties is associated the low carbon content of a lignite. Though the abnormality is generally attributed to the high sulphur content in the coal, the nature of sulphur grouping, however, is not properly understood, and relatively few investigations have been carried out in this direction. For example, I. G. C. DRYDEN and M. GRIFFITH[1] have suggested three possible explanations: formation of SH grouping in coals which are then more mobile than the corresponding compounds containing OH groupings; formation of sulphur–carbon linkages which decompose at a lower temperature than the corresponding carbon–oxygen linkages; or difference in structure from that of normal coals containing oxygen. Based on his studies of the high sulphur coal of Istria, D. J. W. KREULEN[2] has suggested that the excess sulphur replaces carbon in the coal rather than oxygen. He has suggested two possible mechanisms for this transformation: (*i*) commencement of coalification with humic acids of high sulphur and low oxygen content, the abnormal properties resulting because of replacement of oxygen by sulphur; (*ii*) coalification with humic acid with high sulphur and normal oxygen content, with oxygen subsequently splitting off, but unaccompanied by condensation due to the presence of additional rings formed by the sulphur. R. KAVČIČ[3] studied the forms of sulphur present in Raša coal and suggested that sulphur is present mainly in ring structures. J. K. CHOWDHURY *et al.*[4] heated Ledo and Namdung (Assam) coal in a Carius tube with dry acetone and methyl iodide for three days at 110°C and found that sulphur is present as thiols, sulphides and disulphides and also partly in ring structures—about 50 per cent of the total organic sulphur being in the reactive form.

A study of the oxygenated reactive group distribution and coking properties of abnormal coals is of considerable importance in the proper understanding of coal structure and the mechanism of coke formation. In a previous paper[5], the nature of reactive groups in normal coals was discussed. In the present paper this study has been extended to abnormal coals.

The coals selected for this study were from India (Assam), Pakistan[6, 7], Borneo[6], Australia[6–8], and Istria[2]. The analyses of the Assam coals are

XUM

Table 1. Analyses of Assam coals

No.	Sample	Caking index B.S. No.	On dry mineral matter free basis									
			Moisture %	Ash %	V.M. %	F.C. %	C.V. %	C %	H %	N %	O %	S %
1	Namdung	—	1·9	4·50	44·1	55·9	14 380	79·6	5·62	1·44	10·4	2·9
2	Baragolai	7	1·8	2·5	43·5	56·5	14 610	81·1	5·84	1·33	10·6	1·1
3	Laitrengew	—	3·3	13·2	46·4	53·6	—	80·0	5·61	0·84	9·9	3·6
4	Moulong	—	5·5	10·0	43·5	56·5	—	79·7	5·18	1·29	10·1	3·7
5	Bagrakota	—	1·2	41·4	33·7	76·3	—	88·0	4·07	1·85	5·3	—
6	Cherrapunji Mowmulu Hill	25	1·4	10·3	46·4 46·7*	53·6 53·3*	14 930 14 800*	80·8	5·72	0·88	8·9	3·7
7	Cherrapunji Mawsmari Hill	31	2·0	4·3	45·1 45·1*	54·9 54·9*	14 760 14 760*	81·4	5·60	0·85	7·5	4·5
8	Laitrengew	26	1·4	11·5	46·6 46·7*	53·4 53·3*	14 790 14 740*	81·1	5·75	0·95	8·8	3·4
9	Lyngkyrdem	39	1·1	8·0	45·0 45·6*	55·0 54·4*	15 050 14 880*	81·2	5·63	0·98	9·1	3·0
10	Thanjinath	30	1·3	11·3	42·8 43·0*	57·2 57·0*	15 190 15 140*	83·5	5·58	0·98	5·7	4·1

* Indicates values corrected for pyritic sulphur.

Table 2. Reactive groups in abnormal coals

Table 2. Reactive groups in abnormal coals

No.	Sample	C% (d.a.f.)	O% (d.a.f.)	S% (d.a.f.)	Reactive groups corresponding to O%			B.S. Swelling No.	Heat of wetting in methanol cal/g (d.a.f.)
					A	B	C		
1	*Raša, Istria, Croatia*[2]	75·4	6·6	10·9	0·5	1·5	3·0	9	3·2
2	*Thanjinath, Assam, India*	83·5	5·7	3·6	0·2	1·1	2·5	8	4·0
3	*Cherrapunji, Assam, India*	81·4	7·5	4·2	0·8	2·2	3·6	7·5	5·3
4	*Lyngkyrdem, Assam, India*	81·2	9·1	2·7	1·8	4·6	4·6	7·5	3·9
5	*Cherrapunji, Assam, India*	80·8	8·9	3·3	1·6	4·5	4·5	6	5·0
6	*Bundamba, Queensland*[6]	82·4	8·1	1·0	1·1	3·0	4·0	5·5	—
7	*Silimpopon, Borneo*[6]	80·2	8·7	4·9	1·5	4·3	4·4	5·5	—
8	*Khost-Sharig, Pakistan*[7]	74·0	10·0	7·7	2·6	5·3	5·3	5·5	5·0
9	*Laitrengew, Assam, India*	81·1	9·3	3·0	2·0	4·8	4·8	5	4·9
10	*S. Yorks*[8]	80·7	7·4	5·6	0·7	3·6	3·6	5	—
11	*S. Yorks*[8]	82·5	12·0	0·6	5·5	6·8	6·8	4	—
12	*Bintulu, Borneo*[6]	79·4	11·0	2·4	3·9	6·0	6·0	4	—
13	*Khost-Sharig, Pakistan*[6]	77·6	8·5	6·3	1·4	4·3	4·5	3	—
14	*Lithgow, N.S.W.*[8]	81·2	8·8	2·1	1·6	4·4	4·2	2·5	—
15	*Khost-Sharig, Pakistan*[6]	79·3	9·7	1·6	2·4	5·1	5·1	2	—
16	*Sadong, Borneo*[6]	77·1	14·9	0·9	9·0	9·0	9·0	2	—
17	*Trans-Indus, Pakistan*[6]	75·3	14·4	3·2	8·7	8·7	8·7	2	—
18	*S. Yorks*[8]	80·7	11·7	0·6	5·0	6·6	6·6	1·5	—
19	*Trans-Indus, Pakistan*[6]	75·7	12·2	5·2	5·9	7·0	7·0	1·5	—
20	*Trans-Indus, Pakistan*[6]	74·8	13·2	4·8	7·7	7·8	7·8	1·5	—
21	*Salt-range, Pakistan*[6]	74·9	12·4	6·0	5·9	7·0	7·0	1	—
22	*Mach-Bolan, Pakistan*[6]	73·2	12·6	6·6	6·7	7·3	7·3	1	—
23	*Mach-Bolan, Pakistan*[6]	67·9	15·4	10·0	9·3	9·3	9·3	1	—
24	*Salt-range, Pakistan*[7] (*Lignite*)	74·6	13·6	5·5	8·1	8·1	8·1	—	19·8
25	*Mach-Bolan, Pakistan*[7]	73·3	16·3	4·1	10·2	10·2	10·2	—	26·2

given in *Table 1*. The analyses for the other coals were reported by previous workers[2, 6-8], and are given in *Table 2*.

FUNCTIONAL GROUP CONSIDERATIONS

During recent years several workers[9-15] have examined the functional groups present in normal coals of different rank. Their values for hydroxyl, carboxyl and carbonyl groups are graphically represented in *Figures 1* to *3*.

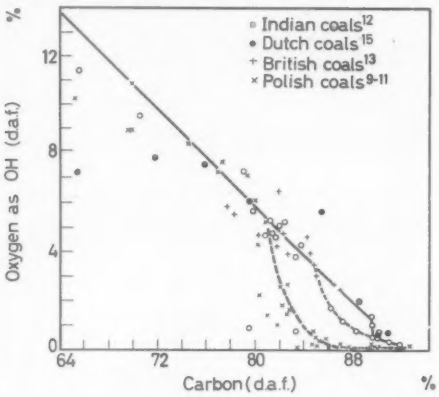

Figure 1. Oxygen as hydroxyl groups in different rank coals

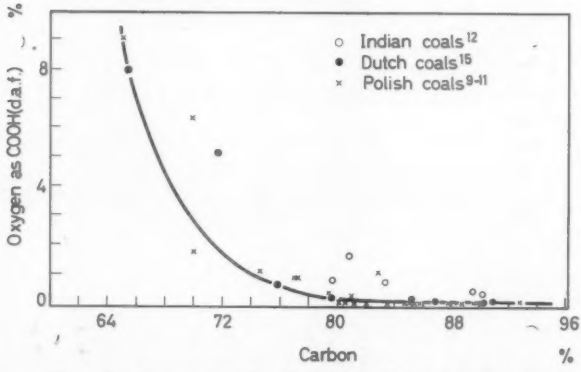

Figure 2. Oxygen as carboxyl groups in different rank coals

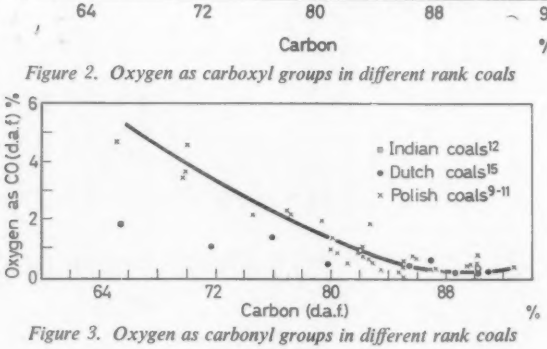

Figure 3. Oxygen as carbonyl groups in different rank coals

Figure 4 represents the total reactive groups in coal as derived from *Figures 1* to *3*.

The *A*, *B* and *C* in *Figure 4* and *Table 2* indicate the break in hydroxyl content as reported by A. IHNATOWICZ and B. ROGA[9-11], B. K. MAZUMDAR[12] and W. F. WYSS[13], respectively. According to Ihnatowicz the hydroxyl content of coal decreases sharply at 80 per cent carbon and above and Wyss reports this at much higher values, 89 per cent carbon and above,

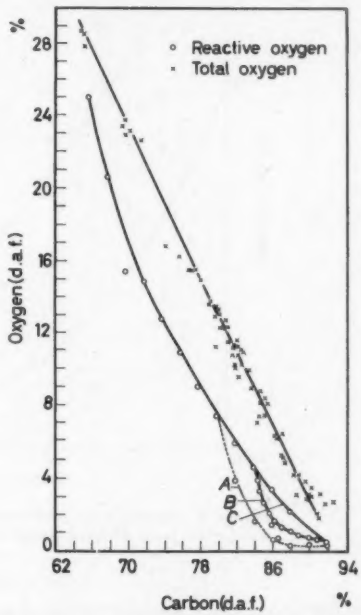

Figure 4. Total reactive oxygen in different rank coals

which is also confirmed by recent work[15]. Mazumdar, however, observes this break at 85 per cent carbon. The difference in observations between the various workers might be due to the wide difference in the petrographic components of coal and the reagents used.

The interesting thing to note from these results is that the development of coking properties corresponds with the disappearance of the carboxyl groups and a reduction of carbonyl and hydroxyl groups, and this does not seem to be accidental.

An examination of *Table 2* shows that in abnormal coals which have developed coking properties, the total amount of reactive oxygen is generally low. The lower the reactive groups, the higher is the swelling index. This is graphically presented in *Figure 5*. Despite the difference in the values of hydroxyl groups (and total reactive groups) the general trend shown is that in abnormal coals high swelling number is associated with lower number of reactive groups. In general, abnormal coals which have developed coking

XUM

properties do not contain carboxyl groups. Their heat of wetting in methanol is also low. On the other hand, most of the Pakistan coals which are non-coking contain appreciable amounts of oxygen as reactive groups. Their heats of wetting are also high. It has been shown previously[5] that the heat of wetting in effect gives a measure of the reactive groups present in coal.

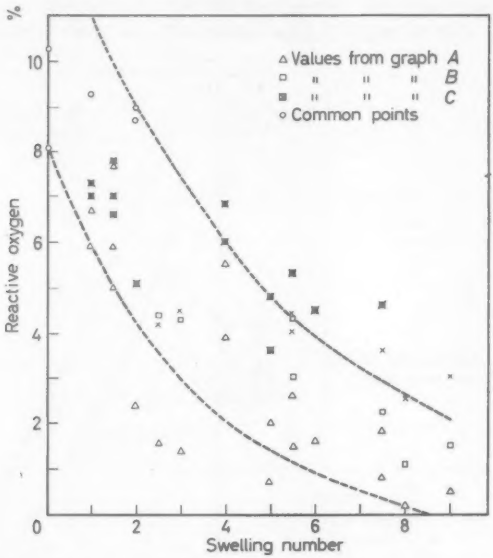

Figure 5. Variation of total reactive groups with swelling number of coals (Values based on Figure 4 and Table 2)

CONCLUSION

From the above discussion, it would appear that abnormal coals which have high swelling number have low reactive oxygenated groups and also low heat of wetting in methanol.

Central Fuel Research Institute,
Jealgora,
Bihar, India

(*Received October 1956*)

REFERENCES

[1] DRYDEN, I. G. C. and GRIFFITH, M. *Mon. Bull. Brit. Coal Util. Res. Ass.* 18 (1954) 63
[2] KREULEN, D. J. W. *Fuel, Lond.* 29 (1952) 462
[3] KAVČIČ, R. *Bull. sci. Yougoslavie* 2 (1954) 12
[4] CHOWDHURY, J. K., DATTA, P. B. and GHOSH, S. R. *J. sci. industr. Res. B* 11 (1952) 150
[5] IYENGAR, M. S. and LAHIRI, A. *Fuel, Lond.* 36 (1957) 286
[6] FRANCIS, W. *J. Inst. Fuel* 24 (1952) 15
[7] BERKOWITZ, N. and SCHEIN, H. G. *Fuel, Lond.* 31 (1952) 19
[8] BROOKS, J. D. *J. Inst. Fuel* 29 (1956) 82

[9] IHNATOWICZ, A. *Komun. No. 125.* Glownego Instytutu Gornictwa: Katowice, 1952
[10] ROGA, B. and IHNATOWICZ, A. *Komun. No. 142.* Glownego Instytutu Gornictwa: Katowice, 1954
[11] ROGA, B. *Komun. No. 152.* Glownego Instytutu Gornictwa: Katowice, 1954
[12] MAZUMDAR, B. K., BHANGALE, P.H. and LAHIRI, A. *Fuel, Lond.* 36 (1957) 307
[13] WYSS, W. F. *Chem. & Ind.* (1956) 1095
[14] *Fuel Research 1955*, p 6. H.M.S.O.; London, 1956
[15] BLOM, L., EDELHAUSEN, L. and VAN KREVELEN, D. W. *Fuel, Lond.* 36 (1957) 135

XUM

Kinetics of the Sorption and Desorption of Methanol on Coal

P. FUGASSI, G. OSTAPCHENKO and R. TRAMMELL

The rate of sorption and desorption of methanol on Pittsburgh Seam coal has been studied at 30°, 35° and 40°C. At constant temperature and at a constant methanol pressure, both processes follow the second order rate equation

$$W = t/(A + Bt)$$

where W is the change in weight at time t; A and B are constants. It is shown that $BW_e = AkW_e^2 = 1$, *where* W_e *is the maximum equilibrium value of W at a given pressure and temperature, and k is the velocity constant. For the sorption process the variation of k with temperature is given by the equation*

$$k \text{ sorption} = 4{\cdot}6 \times 10^{10} \exp(-9\,900/RT)\ [g\ coal]\ [mole\ CH_3OH]^{-1}\ [h]^{-1}$$

The corresponding equation for desorption is

$$k \text{ desorption} = 1{\cdot}5 \times 10^{14} \exp(-15\,600/RT)\ [g\ coal]\ [mole\ CH_3OH]^{-1}\ [h]^{-1}$$

A survey of the literature on the kinetics of gas–solid sorption has been made. It appears that sorption and desorption follow this second order equation if the vapour is a substance whose formula includes oxygen and if the solid is a swelling gel of the polysaccharide or protein type. The similarity of the coal gel to these other swelling gels is noted.

THE sorption of methanol on coal in the vicinity of 35°C is known to be reversible[1]. A sample of coal, held at 35°C, upon which methanol has been sorbed, will upon evacuation return to a weight which is very close to its original weight. The average deviation between the original weight and the weight after desorption is about 0·3 of one per cent. Since the weight of the coal remains constant it seems likely that no significant chemical reaction between the coal and methanol has taken place. The reversibility of methanol sorption on coal and the reproducibility of methanol sorption data have been previously noted for three British coals[2].

The sorption of methanol is being used in the Coal Research Laboratory as a tool to determine changes in the coal structure caused by various treatments of the coal. As a tool, its limitations must be accurately charted and for this reason we have devoted considerable time to working out the kinetics of the sorption and desorption processes.

EXPERIMENTAL

The apparatus consisted of a McBain–Bakr balance, the spring of which was constructed from Ni-Span C wire, 0·005 in. in diameter. The spring was calibrated for loads up to 1·5 g and to that point its response was linear with a spring constant of 4·2 mg/mm extension. The coal sample was carried in a glass bucket hung on the end of the spring. The bucket weight was about 150 mg and the coal samples weighed around 400 mg. With a cathetometer reading to 0·1 mm a precision of about 0·1 per cent could be obtained.

The remainder of the apparatus consisted of a manometer, storage reservoirs for various liquids and the vacuum system. Mercury 'cut-offs' were used throughout. The pumping system consisted of a two-stage mercury diffusion pump backed by the usual mechanical pump. The entire apparatus was enclosed in an air thermostat whose temperature was held constant to $\pm 0{\cdot}1\,^{\circ}C$.

The kinetic work was done on samples of Pittsburgh Seam coal. The coal had been ground by passage through a hammer-mill. The samples used were unsieved; they contained particles which ranged from − 60 to − 300 mesh. The analysis of this coal has been published by R. A. GLENN[3]. Absolute methanol was used as received and stored over a drying agent.

Procedure—Since previous experiments had indicated that alcohol sorption changes the structure of the coal in an irreversible manner, the coal samples were aged until the stable structure was obtained. The new coal sample was evacuated for 24 hours at the end of which time the weight had become constant. The sample was then exposed for a number of days to alcohol vapour.

For following the kinetics of the sorption process, the 'aged' sample was evacuated to constant weight and alcohol vapour at a known pressure admitted to the system. Readings of the spring length were then taken at various time intervals. In our apparatus, the volume of the system was large enough, relative to the size of coal sample used, so that the pressure of alcohol varied only slightly during sorption—approximately 1 mm of mercury at low pressures and 5 mm of mercury at the highest pressures used. The final pressure reading was taken as the pressure to be associated with a given experiment.

For the experiments on desorption, the coal sample was permitted to come to equilibrium with a known pressure of alcohol vapour. At zero time, the system was pumped out and the length of the spring measured at various time intervals.

The apparatus employed has certain limitations which cannot be remedied very easily. In the sorption experiments, alcohol vapour had to be admitted to the system slowly (periods of minutes) to prevent the spring being set in oscillation. The desorption experiments required the alcohol vapour to be pumped out slowly to avoid loss of the powdered coal from the bucket. Both of these effects are equivalent to an error in the time scale. The sorption is, of course, exothermic and the desorption endothermic. The quantities of heat involved are not large and it is believed that the temperature of the coal sample during the sorption experiments is close to thermostat temperature. However, during the desorption experiments heat transfer to the surrounding gas is low especially at low pressures, and the temperature of the coal might be lower than the thermostat temperature. To minimize this effect, only the mechanical pump was used during the desorption experiments. If there is a temperature error, it would be more serious in desorption than in sorption because of the larger energy of activation for the desorption process. Fortunately, the energies of activation for the reactions are not very large; this reduces the error that might be caused by temperature changes.

XUM

RESULTS OF KINETIC EXPERIMENTS

Rate equation—Both the sorption and desorption reactions follow the same rate equation

$$W = t/(A + Bt)$$

In this equation, W is the change in weight (increase for sorption, decrease for desorption) at time t. A and B are constants. According to this equation, the limiting value of W, i.e. the equilibrium value W_e at $t = \infty$, must be $1/B$. The constant A must include the velocity constant. It will be shown later that $A = 1/kW_e^2$ where k is the velocity constant for the process.

Inspection of the equation shows that a plot of t/W versus t should yield a straight line whose equation is $t/W = A + Bt$. In *Figure 1* are shown

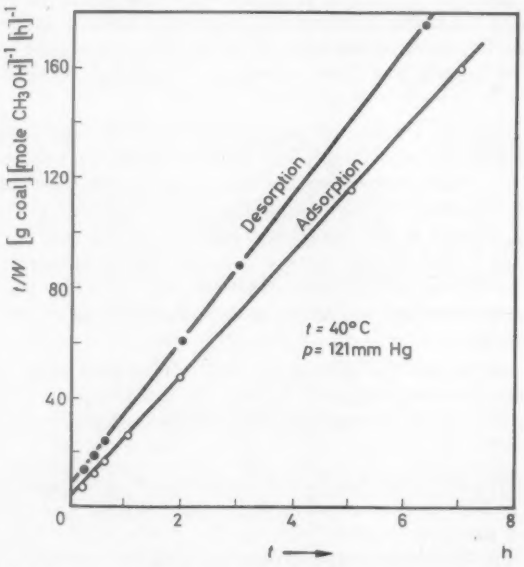

Figure 1. Rate equation plots

plots of adsorption and desorption experiments at 40°C. It will be noticed that all points up to 90 per cent of the reaction fall along the line. For both sorption and desorption experiments the value of W_e, as obtained from the slope of the t/W versus t plot, checks closely with the value of W_e determined at equilibrium. Since the value of W_e determined at equilibrium is independent of heat effects accompanying the sorption or desorption of methanol, it is believed that the temperature of the coal sample is close to the thermostat temperature during the kinetic experiments.

Experimental data—The experimental data are tabulated in *Table 1*. In this table c is the relative pressure and k is the velocity constant. W_e is the equilibrium sorption.

The constant '*A*'—Experimentally, in the sorption experiments at any one temperature, the value of A increases as the pressure increases. It has been found that a value of the velocity constant at a given temperature, independent of the pressure, could be obtained by use of the equation

$$k = 1/A\ W_e^2$$

In *Figure 2* a plot of $1/A\ W_e^2$ as a function of the pressure at 30°C is given for sorption and desorption experiments. The value of k is a constant to

Table 1. Kinetic and equilibrium data

Temp. °C	c	$W_e \times 10^4$ *mole* g^{-1}	k (*sorption*) [*g*] [*mole h*]$^{-1}$	k (*desorption*) [*g*] [*mole h*]$^{-1}$
30	0·089	6·66	4050	940
30	0·273	10·46	3640	870
30	0·476	12·68	3530	590
30	0·672	13·95	3100	770
30	0·881	16·17	3240	1060
35	0·084	6·34	7130	1760
35	0·228	9·83	3720	1330
35	0·282	10·46	5310	1220
35	0·714	14·59	5400	1250
35	0·874	15·22	5110	—
40	0·087	6·98	5520	1820
40	0·122	8·24	—	1610
40	0·283	10·15	5030	—
40	0·303	10·78	7450	1930
40	0·476	12·05	6760	2780
40	0·870	16·49	6170	1670

about 15 per cent. It should be mentioned that experiments at the lower pressures are the least accurate because of the small total change in weight.

Energies of activation—The energies of activation are obtained by plots of log k against the reciprocal of the absolute temperature. The plots for the

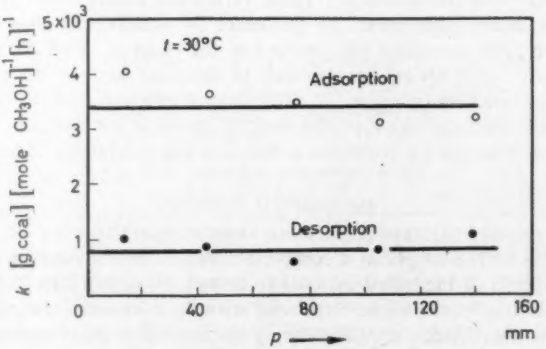

Figure 2. Plot showing independence of k and p

sorption and desorption processes are shown in *Figure 3.* From these plots, the following values are obtained:

k sorption $= 4{\cdot}6 \times 10^{10} \exp(-9\,900/RT)$ [g coal] [mole $CH_3OH]^{-1}$[h]$^{-1}$

k desorption $= 1{\cdot}5 \times 10^{14} \exp(-15\,600/RT)$ [g coal] [mole $CH_3OH]^{-1}$[h]$^{-1}$

The energies of activation for sorption and desorption are respectively 9 900 cal and 15 600 cal. The difference between these two values, − 5 700 cal (exothermic), is the heat of reaction. The low value of the heat of reaction is additional evidence that alcohol sorption is a physical process. E. DRESEL,

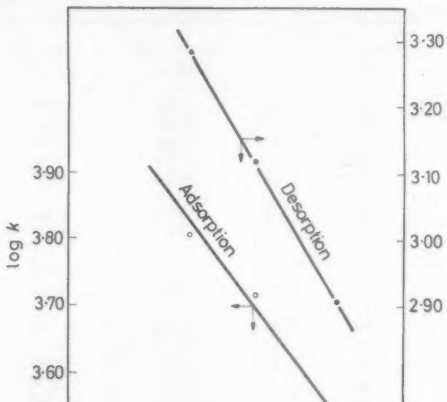

Figure 3. Arrhenius plots for energies of activation

M. GRIFFITH and W. HIRST[2], working with three British coals, reported thermodynamic sorption heats for methanol as determined from the change of the equilibrium sorption with temperature changes ranging from − 13 500 cal/mole to − 10 100 cal/mole. These values are about twice that reported here. The exact significance of the value of − 5 700 cal depends on the mechanism used to explain the kinetics of the process. For the mechanism given below, − 5 700 cal corresponds to the heat of reaction of the rate-determining reaction (reaction 2). The heat of reaction, determined thermodynamically, includes not only the heat of reaction for reaction 2 but also the heats of reaction for reactions 1 and 3 of the postulated mechanism.

EQUILIBRIUM ISOTHERM

Since the velocity constant requires an experimental value for W_e, the equilibrium value of the sorption, a complete solution of the kinetics of sorption and desorption of methanol on coal in closed, equation form, requires that the equilibrium isotherm be expressed also in a closed form. In general, there is no theoretical equation for 'S-shaped' adsorption isotherms which fit the entire pressure range.

We have investigated many types of relationships to obtain empirical equations relating the equilibrium adsorption, W_e, with the relative pressure c. Two equations have been found to be suitable. The first equation is

$$1/W_e = \alpha' + \beta' c + \gamma' c^3 + \delta'/c^3$$

where W_e = equilibrium sorption, c = relative pressure = p/p^0 where p is the pressure of alcohol vapour and p^0 is the vapour pressure of alcohol at the temperature in question, and α', β', γ', δ' are constants. The equation was derived by I. LANGMUIR[4] using a kinetic mechanism and assuming that n molecules were adsorbed on one site. The same equation was derived in a different manner by M. DOLE[5]. The equation as derived is in the form of an infinite series; we have only used terms up to c^3. The equation is perfectly general. By making various assumptions concerning the constants it can be reduced to the BET equation, to the Langmuir adsorption isotherm for monomolecular adsorption, etc. It is possible to fit our equilibrium data to an equation of this form at the three temperatures, 30°, 35° and 40°C. However, the variations of the constants with temperature are erratic and fit no simple equation. For this reason, we prefer to use the second equation which is

$$W_e = \alpha c/(1 + \beta c) + \gamma c/(1 - \delta c) \text{ [mole g}^{-1}\text{]}$$

The symbols have the same meaning as before. The equation also involves four adjustable constants: α, β, γ, δ. This equation is a slightly modified variation of the one derived by A. J. HAILWOOD and S. HORROBIN[6]. The Hailwood–Horrobin equation was used to fit sorption data for water on various types of natural gels of the swelling type. It is suitable, for example, for the sorption of water on silk, cotton, cellulose, wool and gelatin. The origin of the equation is as follows. Sorption of a substance like water on a swelling gel is considered to be divisible into two parts. One part, given by the first term of the equation, represents adsorption of one molecule on

Table 2. Values of constants: Hailwood–Horrobin equation

t°C	α	β	γ	δ
30	0·0133	9·83	$2{\cdot}18 \times 10^{-4}$	+ 0·57
35	0·0140	12·52	$2{\cdot}74 \times 10^{-4}$	+ 0·64
40	0·0192	17·52	$3{\cdot}38 \times 10^{-4}$	+ 0·56

$\log \alpha = -1520/T + 3{\cdot}141$ (7000 cal)
$\log \beta = -2403/T + 8{\cdot}920$ (11 000 cal)
$\gamma = 1{\cdot}21 \times 10^{-5} T - 2{\cdot}44 \times 10^{-3}$
δ = constant (independent of T)
T is expressed in °K

one active site. This portion of the sorption is characterized by relatively high heats of reaction. The second part is assumed to be solution of the water in the gel. The solution is assumed to be ideal and, in fact, the second term is closely related to Raoult's law. That part of the sorption due to ideal solution has zero heat of reaction.

XUM

The Hailwood–Horrobin equation fits our equilibrium data for methanol on coal. Furthermore, the constants vary in a simple manner as the temperature is changed: α and β follow an exponential form, γ follows a linear form, δ appears to be independent of temperature. This is the behaviour that one would anticipate. The values of the constants at the different temperatures, together with the equations relating these constants to temperature, are listed in *Table 2*.

For reasons which will become apparent later, it was necessary to investigate the form of the Hailwood–Horrobin equation for that case where one molecule is held on two sites. With this assumption, it can be shown that only the first term is changed and that the change involves replacing c in this term by $c^{\frac{1}{2}}$. Attempts were made to fit the experimental data to an equation of this form. However, the fit was poor and it seems probable that the sorption equilibrium data require the assumption that one molecule is sorbed on one site.

REACTION MECHANISM

No reaction mechanism can be shown to be a unique solution of a given set of experimental data. As a matter of fact, many different mechanisms can be postulated. In setting up a mechanism for the sorption–desorption process, we will discuss in detail the mechanism for the sorption process. The mechanism for the desorption process will be the reverse of the one postulated for sorption.

In setting up the reaction mechanism for sorption, we have made this mechanism conform to three requirements: (1) explanation of the second order kinetic equation; (2) explanation of the equilibrium equation; and (3) use of a minimum number of equations. The last requirement is, in a sense, artificial. The mechanism we suggest for the sorption process is:

$$CH_3OH\,(g) + S \rightleftharpoons S \cdot CH_3OH \quad \ldots.[1]$$

$$S \cdot CH_3OH + 2\,D \longrightarrow 2(D \cdot \tfrac{1}{2}CH_3OH) + S \quad \ldots.[2]$$

$$S \cdot CH_3OH + 2(D \cdot \tfrac{1}{2}CH_3OH) \rightleftharpoons 2(D \cdot CH_3OH) + S \quad \ldots.[3]$$

Reaction 1 represents the adsorption of alcohol vapour on surface sites, S, on the coal. This type of reaction is known to be rapid and is so marked by the double arrow. A reaction of this kind is essential since adsorption of alcohol on the surface of the coal must precede any subsequent reaction.

Reaction 2 is the slow and rate-determining step of the mechanism. An alcohol molecule leaving the surface and moving into the interior meets, and is held on, a double site, $2D$. Note that, because of the limited dimensions of the alcohol molecule, the two units making up the double site must be close together. A reaction of this type is necessary to account for the observed second order kinetic equation.

Reaction 3 is a rapid reaction (double arrow) whereby a double site holds an additional alcohol molecule. This reaction is necessary to explain the sorption equilibrium equation requiring that the sorption be a function of c and not of $c^{\frac{1}{2}}$.

From the mechanism, it can be shown that the differential equation for the sorption of methanol on coal is

$$\frac{dW}{dt} = \frac{k K_1 p}{1 + K_1 p} W_e^2 \left(1 - \frac{W}{W_e}\right)^2$$

In this equation, k is the velocity constant, K_1 is the equilibrium constant for the adsorption of methanol on surface sites S, W_e the equilibrium sorption, and W the sorption at time t.

The term W/W_e represents the fraction of the sites which are occupied by sorbed alcohol molecules at time t. The term $[1 - (W/W_e)]$ is therefore the fraction of sites which are vacant at time $t = t$. The rate then involves the square of the fraction of vacant sites.

We will now consider how a single molecule can occupy two adjacent sites. There are only two possibilities:

(*1*) The molecule dissociates into two parts, each part being held by a single site;

(*2*) The molecule has dimensions sufficiently large to cover two sites.

Dissociation is known to occur for the adsorption of certain diatomic molecules, such as H_2, on metals. If this behaviour is postulated for methanol the methanol molecule must dissociate into two dissimilar fragments. Energy considerations make it unlikely that the fragments are ions. Therefore, the fragments must be free radicals such as CH_3 and OH. Free radicals are very reactive. It is difficult to see how the free radicals could avoid reacting with coal (giving irreversible sorption) or avoid reacting with each other to give molecules other than CH_3OH (resulting in decomposition of the alcohol). It seems reasonable to conclude that free radicals are not involved and that the alcohol molecule is sorbed as an entity on two adjacent sites.

Now, actually for our sorption rate data, we have used the equation

$$\frac{dW}{dt} = k_x W_e^2 \left(1 - \frac{W}{W_e}\right)^2$$

This means that over the pressure region used in our experiments $K_1 p$ is much greater than unity so that the term, $K_1 p/(1 + K_1 p)$ is 1. At very low pressure, this will not be true and the apparent velocity constant, k_x, should depend on the pressure. However, experiments in this region would be difficult to do because the total sorption at these pressures will be small. Experimentation in the low pressure region will require a balance considerably more sensitive than the one now being used.

For desorption experiments, the mechanism requires the equation

$$-\frac{dW}{dt} = k' \cdot \frac{1}{1 + K_1 p} \cdot W_e^2 \cdot \left(\frac{W}{W_e}\right)^2$$

Here the rate of desorption is proportional to the square of the fraction of

XUM

occupied sites. Actually, our rate constants are calculated from the equation

$$-\frac{dW}{dt} = k_x' \cdot W_e^2 \cdot \left(\frac{W}{W_e}\right)^2$$

It is apparent that under our conditions where p is kept at a value around 10^{-2} mm of mercury our experimental velocity constant for desorption, k_x' is really k'. During the desorption, with p at a low value, the term $(1 + K_1 p)$ will essentially be unity.

Although the sorption occurs on S sites and D sites, the reaction kinetics show that the total weight, which is the experimental quantity actually measured, is, at time t, an accurate measure of occupied D sites. This means that the amount of adsorption on S sites must be considerably less than the sorption on D sites. The surface area of coal is then either very large with a low concentration of S sites or small with a high concentration of S sites. The kinetic data tell us nothing about the surface area of coal.

In talking about the mechanism, we have, for convenience, distinguished the two types of sites, S and D, by calling S sites surface sites, and D sites interior sites. It should be pointed out that S and D sites could, in reality, be surface sites located at the solid/gas interface. The D sites would differ from the S sites by their geometrical position. D sites might be located on the sides or bottom of very small capillaries through which methanol molecules move with difficulty. Although we have not considered this second picture in detail, we favour, at this time, the concept of surface and interior sites.

DISCUSSION

The physical dimensions of the methanol molecule are small. Using a scale model, it can be shown that the methanol molecule fits easily in a cube of 4 Å side. It seems likely that the double sites, $2D$, postulated in the mechanism are atoms and that such atoms must be sufficiently close to accommodate the small dimensions of the methanol molecule. The question to be solved is what type of atoms in coal are responsible for methanol adsorption.

The five principal elements in coal, in decreasing percentages, are carbon, oxygen, hydrogen, nitrogen and sulphur. In the sample of Pittsburgh Seam coal used in these experiments, these elements are present in the following amounts, expressed as moles of atoms per gramme of coal: $C = 65 \times 10^{-3}$, $O = 4 \times 10^{-3}$, $H = 47 \times 10^{-3}$, $N = 1 \times 10^{-3}$, $S = 0{\cdot}3 \times 10^{-3}$. Now, using only the first term of the Hailwood–Horrobin equation, the maximum number of sites needed in terms of moles of sites per gramme of coal are:

$1{\cdot}23 \times 10^{-3}$ at 30°C, $1{\cdot}03 \times 10^{-3}$ at 35°C, and $1{\cdot}04 \times 10^{-3}$ at 40°C.

Comparing these values with the preceding values for the coal, we can see that the elements which could furnish the sites for alcohol adsorption are carbon, hydrogen or oxygen if we say the sites are made up of a single type of element. In view of the chemistry of methanol with its OH group, it would seem likely that the oxygen atoms in coal are the ones involved in methanol sorption.

It appears that sorption of methanol by coal involves diffusion and that such a process should obey Fick's law. The special conditions under which Fick's law would reduce to the simple second order experimental equation are not known, but it is obvious that the experimental equation is not a general solution of Fick's law. For this reason, it seems desirable to examine the experimental kinetic data in the literature for various solids and various gases to determine the nature of the system to which the second order equation applies. Such data are scanty and incomplete so that any conclusions to be drawn are tentative ones, based on one or two sets of experimental data. A complete kinetic analysis would be desirable but such detailed studies must be left to the future.

A summary of the results obtained to date is given in *Tables 3* and *4*.

Table 3. Systems which do not fit second order equation

Alcohols on keratin	*Amines on coal, rubber, or sulphur*
Methylene chloride on cellulose acetate	*Carbon disulphide on coal*
Propane on polyisobutylene	*Methyl iodide on coal*
Benzene on rubber	*Water and alcohols on wool*

Table 4. Systems which do fit second order equation

Water on wool, gelatin, cellulose acetate, egg albumin, coal
Alcohols on coal, cellulose acetate, cellulose
β-Methoxyethylamine on low rank coals and certain high rank coals

Inspection of *Table 3* and *Table 4* shows that the second order equation is followed by gases having the formula *R*OH, such as H_2O, CH_3OH and other alcohols and one gas, β-methoxyethylamine, with the grouping *R*OCH_3. It will be noted that wool appears in both tables. The rate data of G. KING and A. B. D. CASSIE[7] for sorption on wool do not follow the second order equation. On the other hand, the rate data given by H. B. BULL[8] for water on wool do follow the rate equation. Wool is a protein, crosslinked by easily broken disulphide bonds. It is possible that the apparent discrepancy is caused by wool samples crosslinked to different degrees. It will be noted that coal falls in with gelatin, cellulose and other swelling gels.

The data on β-methoxyethylamine are extensive but conflicting. On lower rank coals the rate of sorption of β-methoxyethylamine follows the second order equation. The same equation is also followed by a few higher rank coals. On cellulose, the behaviour of β-methoxyethylamine is also unusual. The sorption on fresh cellulose does not follow the second order equation, but if the cellulose sample is 'aged' by exposure to β-methoxyethylamine vapour, the sorption data on the 'aged' cellulose do follow the second order equation. Further work might show that this type of behaviour is true for some coals also.

It has been pointed out that the coal gel has many of the characteristics of swelling gels such as cellulose. Compare the sorption of methanol on cellulose with the sorption of methanol on coal. Both processes follow rate

XUM

equations which are identical in form and seem to reach equilibrium conditions in each case, which likewise seem related in form. The question is, why both coal and cellulose seem to be identical from the standpoint of the methanol molecule. It seems probable that the methanol molecule cannot distinguish between coal and cellulose, because in both types of gels the forces between adjacent polymer units are identical. Such identity of forces probably arises because in both coal and cellulose there occurs either the same functional group or two closely related functional groups. The problem, then, from this standpoint, is to investigate the limited number of types of functional groups present in the known structure of cellulose and to decide which group, or which types of groups, could be common to both coal and cellulose. Since it is known that polymeric hydrocarbons show little or no adsorption of water, alcohol and similar polar molecules, it seems probable that the active sites for alcohol sorption on cellulose and coal must involve oxygen in some way.

In summary, it can be said that the coal gel, or one of the gels involved in coal, if it is a mixture of gels, appears to be closely related in properties to other swelling gels such as cellulose. It appears to be safe to conclude that the forces holding such gels together are similar and are hydrogen bonding and van der Waals forces. Evidence has been presented to suggest the hypothesis that the similarity of these gels is due to the presence in each gel of oxygen and carbon atoms joined together in certain arrangements. It is suggested that the functional group, or groups, involved is, or are, common to these gels.

Coal Research Laboratory,
Department of Chemistry,
Carnegie Institute of Technology,
Pittsburgh 13, Pa.

(*Received February 1957*)

REFERENCES

[1] FUGASSI, P., HUDSON, R. and OSTAPCHENKO, G. *Fuel, Lond.* 37 (1958) 25
[2] DRESEL, E., GRIFFITH, M. and HIRST, W. *Trans. Faraday Soc.* 44 (1948) 992
[3] GLENN, R. A. *Fuel, Lond.* 34 (1955) 202
[4] LANGMUIR, I. *J. Amer. chem. Soc.* 40 (1918) 1375
[5] DOLE, M. *J. chem. Phys.* 16 (1948) 25; *Ann. N.Y. Acad. Sci.* 51 (1949) 705
[6] HAILWOOD, A. J. and HORROBIN, S. *Trans. Faraday Soc.* 47B (1946) 84
[7] KING, G. and CASSIE, A. B. D. *Trans. Faraday Soc.* 36 (1940) 445
KING, G. *Trans. Faraday Soc.* 41 (1945) 325
[8] BULL, H. B. *J. Amer. chem. Soc.* 66 (1944) 1499

An Investigation into Methods for the Determination of Forms of Sulphur in Coal

A. H. EDWARDS, G. N. DAYBELL and W. J. S. PRINGLE

The methods of the British Standards Institution, the Fuel Research Board, and the British Coke Research Association for the determination of forms of sulphur in coal have been investigated. The accuracy of the 'non-simultaneous' procedure of the F.R.B. method, the B.S. and B.C.R.A. methods has been confirmed. The B.C.R.A. method is shown to give the most accurate results. The conclusion of Teichmann is confirmed that there is some oxidation of pyrites by a protracted hydrochloric acid process for the determination of non-pyritic iron. A proposed modification to the F.R.B. and B.C.R.A. methods, involving introduction of a colorimetric technique for the estimation of iron, is demonstrated to be acceptable and to have decided advantages over the standard volumetric techniques.

SULPHUR normally exists in coal in three forms: as sulphates (generally of iron and calcium), as iron pyrites, and in organic combination within the coal substance. In most schemes of coal analysis the first two of these sulphur forms are determined by analytical methods and the third—the organic sulphur—is taken to be the difference between the total sulphur and the sum of the sulphate and pyritic sulphur.

The first comprehensive study of the determination of sulphur forms was made by A. R. POWELL and S. W. PARR[1] in 1919, and the methods specified in *British Standards Specification 1016*[2] and in *Survey Paper No. 44* of the Fuel Research Board[3] are based on that work. Powell and Parr determined organic sulphur directly but their methods were very lengthy and unsuited to routine operation. A. R. POWELL[4] showed that, for six coals, the difference between total sulphur and the sum of sulphate and pyritic sulphur represented sulphur present in an organic form, and recommended that this difference should be reported as organic sulphur in rapid routine work. This method of calculation is used in both British methods mentioned above.

The B.S. method makes use of the assumption that treatment of coal with dilute hydrochloric acid at 60°C for 40 hours results in solution of sulphate sulphur but leaves pyritic and organic sulphur unaffected, whereas dilute nitric acid at room temperature dissolves both sulphate sulphur and pyritic sulphur without attacking organic sulphur; estimation of the sulphur in these two acid extracts therefore affords a means of determining the sulphate and pyritic sulphur contents of the sample. The F.R.B. method employs the same acid extractions to bring sulphate and pyritic sulphur into solution but recommends that the pyritic sulphur in the nitric acid extract be determined as pyritic iron and converted to the corresponding pyritic sulphur

XUM

value by the factor appropriate to the formula FeS_2 for pyrites. This modification was suggested by the findings of Powell[4] that the nitric acid treatment can bring about oxidation and solution of some organic sulphur in certain coals, and that it was therefore erroneous to assume that all the sulphur in the nitric acid extract invariably originated only from the sulphates and pyrites in the sample. The work of M. J. BUERGER[5] and P.E. ROUSSEAU[6] serves to confirm the assignment of the formula FeS_2 to pyrites in coal.

Both the B.S. and F.R.B. methods are time consuming, and the danger that the specified prolonged extraction with dilute hydrochloric acid may result in some oxidation and solution of pyrites has been pointed out by J. TEICHMANN[7]. He suggested that the danger can be averted by the use of stronger acid at boiling point for a much shorter period (one hour), and claimed that complete extraction of sulphate sulphur is effected by that procedure. More recently the British Coke Research Association (*vide* R. A. MOTT[8]) has suggested further modifications and advocated that both hydrochloric acid and nitric acid extractions be carried out at boiling point with reduction of the extraction periods to 30 minutes.

The Coal Survey Branch of the Scientific Department of the National Coal Board includes the determination of sulphur forms in its routine analysis of coal, and it has undertaken an examination of the B.C.R.A. method and of a number of difficulties that have arisen in the application of the B.S. and F.R.B. methods. Nine coals have been examined by all three methods. The coals covered a range of rank from Coal Rank Code Nos.

Table 1. Proximate analyses, sulphur contents and coke types of samples

Division	*North-ern (N & C)*	*Durham*	*Durham*	*East Mid-lands*	*Scottish*	*Scottish*	*Scottish*	*Durham*	*Durham*
Seam or type	*Cobbles*	*Busty seam*	*'B' seam*	*Eureka seam*	*Major seam*	*Maid seam*	*Major seam*	*Old Five Quarter seam*	*Hutton seam*
Sample numbers	10641	10642	10653	10660	10670	10671	10672	10679	10680
Proximate analysis (*air-dried coal: per cent*)									
Moisture	7·3	1·1	1·3	12·3	5·0	3·7	1·9	1·3	1·7
VM less moisture	35·6	26·9	22·9	35·8	35·3	29·5	26·6	32·5	32·8
Fixed carbon	52·4	65·6	56·4	44·1	51·1	45·4	60·2	59·6	59·3
Ash	4·7	6·4	19·4	7·8	8·6	21·4	11·3	6·6	6·2
VM (dry, ash-free coal: per cent)	40·4	29·1	28·8	44·8	40·8	39·4	30·6	35·3	35·6
Total sulphur (air-dried coal: per cent)	1·91	1·14	1·51	3·33	1·54	1·37	4·28	2·51	2·44
Gray–King coke type	*G–G1*	*G7*	*G5*	*B*	*E*	*B*	*B*	*G1*	*G7*
Coal Rank Code	602–702	301	300	902	702	902	901	401*b*	501*b*

300 to 900 and had total sulphur contents ranging from 1·1 per cent to 4·3 per cent (*Table 1*). The results obtained form the subject of this paper.

A completely different method of determining pyritic sulphur proposed by L. W. MANTEL and W. RADMACHER[9] and later modified by W. RADMACHER and P. MOHRHAUER[10] to overcome certain difficulties reported by R. BELCHER and C. E. SPOONER[11] has also been assessed. It is based on reduction of pyrites by nascent hydrogen and estimation of the hydrogen sulphide produced. The modified method appears to work satisfactorily but has the disadvantage that the coal sample must be reduced to a maximum particle size of about 15 microns. The method has not been extensively investigated and it is not considered in this paper.

EXAMINATION OF THE B.S. AND F.R.B. METHODS

The following points have been investigated for the B.S. and F.R.B. methods on the nine coals selected for the investigation:

(*a*) the effect of using coal ground to — 72 B.S. mesh instead of to — 120 B.S. as specified;

(*b*) the use of mercurous nitrate as an alternative to a titanous reagent for the titration of iron in the F.R.B. method;

(*c*) the equivalence of the 'simultaneous' and 'non-simultaneous' procedures for the determination of pyritic sulphur by the F.R.B. method; and

(*d*) the equivalence of the B.S. and F.R.B. methods.

(*a*) *The effect of using — 72 B.S. mesh coal*

Both methods specify that the coal sample should be ground to pass a 120 B.S. mesh sieve. Most routine coal analysis is carried out on B.S. 72-mesh material and it would obviously be an advantage if material of that size proved suitable for this determination.

Sulphate and pyritic sulphur determinations were made on the nine selected samples by one of the standard methods (the F.R.B. non-simultaneous procedure) using samples ground to both sizes. The results, which are given in columns (A) and (B) of *Table 2*, demonstrate that identical values are obtained from the two sizes.

Since the B.S. method is fundamentally similar to the F.R.B. method, it can be assumed that the use of — 72 B.S. mesh material in the B.S. method will also give satisfactory results.

(*b*) *The use of mercurous nitrate*

In the original Powell and Parr method, iron determinations were made by a permanganate titration, which required prior reduction of the iron to the ferrous state. To avoid the latter step the F.R.B. method recommends the use of a titanous reagent (sulphate or chloride) for the titration of iron. R. BELCHER and C. E. SPOONER[11] pointed out that mercurous nitrate is a suitable reagent for the direct titration of ferric iron, according to the method of F. R. BRADBURY and E. G. EDWARDS[12] and that it is preferable to titanous reagents as it needs no special storage precautions.

XUM

In several Coal Survey Laboratories it has been observed that the end point of mercurous nitrate titrations in nitric acid is occasionally very poor, in that the red coloration due to ferric thiocyanate may return very shortly after the colourless end point has been reached. When such determinations are repeated and a normal end point obtained, the first result is invariably higher than the second.

It was thought that this difficulty may be caused by nitrogen oxides in the solution produced by the reaction between nitric acid and coal. R. BELCHER

Table 2. Sulphate, pyritic and organic sulphur given by different methods

Form of sulphur	*F.R.B. method: 'non-simultaneous' procedure (per cent sulphur)*			*F.R.B. method: 'simultaneous' procedure (per cent sulphur)*		*'Non-simultaneous' procedure: B.S. method (per cent sulphur)*	*B.C.R.A. method: (per cent sulphur)*
	B.S. 120-mesh coal titanous sulphate (A)	*B.S. 72-mesh coal titanous sulphate (B)*	*B.S. 72-mesh coal mercurous nitrate (C)*	*B.S. 72-mesh coal mercurous nitrate*	*B.S. 72-mesh coal titanous sulphate*	*B.S. 72-mesh coal*	*B.S. 72-mesh coal*
Sulphate (as sulphur)							
10641	0·02	0·02	0·02	0·02	0·02	0·02	0·02
10642	0·03	0·03	0·03	0·03	0·03	0·03	0·02
10653*	0·06	0·06	0·05	0·06	0·06	0·06	0·04
10660*	0·09	0·09	0·10	0·08	0·08	0·08	0·10
10670	0·02	0·02	0·03	0·02	0·02	0·02	0·03
10671*	0·02	0·02	0·02	0·02	0·02	0·02	0·02
10672	0·13	0·11	0·12	0·11	0·10	0·11	0·09
10679	0·03	0·03	0·03	0·03	0·03	0·03	0·01
10680*	0·22	0·22	0·22	0·22	0·21	0·23	0·19
Pyritic							
10641 *from Fe*	0·90	0·91	0·90	0·91	0·90		0·90
10641 *as $BaSO_4$*		0·89	0·90			0·87	
10642 *from Fe*	0·54	0·55	0·54	0·53	0·53		0·56
10642 *as $BaSO_4$*		0·52	0·54			0·51	
10653* *from Fe*	0·76	0·77	0·77	0·57	0·57		0·79
10653* *as $BaSO_4$*		0·76	0·77			0·75	
10660* *from Fe*	2·31	2·35	2·38	2·22	2·23		2·24
10660* *as $BaSO_4$*		2·37	2·34			2·28	
10670 *from Fe*	0·69	0·69	0·69	0·69	0·70		0·67
10670 *as $BaSO_4$*		0·69	0·69			0·68	
10671* *from Fe*	0·69	0·70	0·69	0·46	0·47		0·71
10671* *as $BaSO_4$*		0·68	0·67			0·68	
10672 *from Fe*	2·57	2·62	2·59	2·61	2·59		2·67
10672 *as $BaSO_4$*		2·57	2·52			2·53	
10679 *from Fe*	1·19	1·20	1·17	1·17	1·18		1·22
10679 *as $BaSO_4$*		1·18	1·15			1·16	
10680* *from Fe*	1·03	1·04	1·03	0·94	0·93		1·10
10680* *as $BaSO_4$*		1·04	1·04			1·01	
Organic (*calc.*)							
10641 (*a*)	0·99	0·98	0·98	0·98	0·98		0·99
10641 (*b*)		1·00	0·99			1·02	
10642 (*a*)	0·57	0·57	0·58	0·58	0·58		0·56
10642 (*b*)		0·59	0·58			0·60	
10653* (*a*)	0·70	0·68	0·69	0·89	0·88		0·68
10653* (*b*)		0·70	0·69			0·71	
10660* (*a*)	0·93	0·89	0·86	1·03	1·02		0·99
10660* (*b*)		0·87	0·89			0·97	
10670 (*a*)	0·84	0·83	0·83	0·84	0·83		0·84
10670 (*b*)		0·73	0·83			0·85	
10671* (*a*)	0·66	0·66	0·66	0·89	0·88		0·65
10671* (*b*)		0·68	0·68			0·68	
10672 (*a*)	1·58	1·54	1·57	1·56	1·58		1·51
10672 (*b*)		1·60	1·64			1·63	
10679 (*a*)	1·28	1·28	1·31	1·31	1·30		1·28
10679 (*b*)		1·30	1·33			1·31	
10680* (*a*)	1·18	1·17	1·18	1·28	1·29		1·15
10680* (*b*)		1·17	1·17			1·19	

(*a*) Derived from pyritic sulphur calculated from pyritic iron.
(*b*) Derived from pyritic sulphur determined as $BaSO_4$.
* Higher pyritic iron by 'non-simultaneous' procedure than by the 'simultaneous' procedure.

(with T. R. WEST[13]) asserts that nitrite ions, even in very small amounts, interfere with the mercurous nitrate titration due to the formation of nitrosyl thiocyanate. The effect of oxides of nitrogen on the titration of iron by mercurous nitrate was established by experiments in which 20 ml of approximately N/55·84 ferric ammonium sulphate solution was titrated against approximately N/55·84 mercurous nitrate solution in 5 per cent nitric acid and in the presence of various amounts of a 0·01 per cent solution of sodium nitrite (in acid solution the nitrite ion decomposes to oxides of nitrogen). The results are given in *Table 3.*

Table 3. Effect of nitrite ions on mercurous nitrate titration

Added 0·01% sodium nitrite solution (ml)	*Equivalent of nitric oxide* (NO) *(mg)*	*Mercurous nitrate titre (ml)*	*Time for pink colour to return (min)*
Nil	*Nil*	20·30	*Over* 60
2	0·09	20·35	8
4	0·17	20·55	6
7	0·30	20·80	1·5
10	0·43	24·50	*At once*

Interference by these oxides appears to arise from re-oxidation of reduced iron. It can be prevented and sharp end points obtained by boiling the solution for 15 minutes before titration to remove oxides of nitrogen.

The nine selected coals were examined for pyritic iron by the F.R.B. method and using both titanous sulphate and mercurous nitrate (with the above precaution) for the titration. The results shown in *Tables 2* and *4* confirm the acceptability of mercurous nitrate as a reagent for the determination of ferric iron.

(*c*) *Equivalence of F.R.B. 'simultaneous' and 'non-simultaneous' procedures*
The F.R.B. method allows two procedures for the determination of pyritic sulphur. The essential difference between them is that in one the pyritic iron is determined directly on the nitric acid extract of coal which has previously been extracted with dilute hydrochloric acid for the sulphate sulphur determination, whereas in the other a fresh portion of coal is used for nitric acid extraction and the value for pyritic iron obtained by subtracting the iron found in the hydrochloric acid extract (the 'non-pyritic' iron) from the iron found in the nitric acid extract ('total acid-soluble' iron). The former is referred to as the 'non-simultaneous' procedure and the latter as the 'simultaneous' procedure.

It is implied that the two procedures are equivalent. This can be so only if the amount of iron extracted from fresh coal by the nitric acid treatment (i.e. the 'total acid-soluble' iron) is equal to the amount extracted by successive treatment with hydrochloric acid and nitric acid (i.e. the 'non-pyritic' and 'pyritic' iron). That this is not invariably true is demonstrated

XUM

Table 4. Sulphur balances for different methods

Sample number	Total sulphur (Eschka method)	Form of sulphur	F.R.B. method: 'non-simultaneous' procedure				B.C.R.A. method	
			Iron titrated with mercurous nitrate		Iron titrated with titanous sulphate		Iron titrated with potassium dichromate	
			Pyritic sulphur estimated from Fe per cent	Pyritic sulphur estimated as $BaSO_4$ per cent	Pyritic sulphur estimated from Fe per cent	Pyritic sulphur estimated as $BaSO_4$ per cent	Pyritic sulphur estimated from Fe per cent	Pyritic sulphur estimated as $BaSO_4$ per cent
10641	1·909	*Sulphate*	0·023	0·023	0·022	0·022	0·021	0·874
		Pyritic	0·902	0·897	0·906	0·892	0·896	
		Organic	1·006	1·006	1·005	1·005	0·928	0·928
		Total (calc.)	1·931	1·926	1·933	1·919	1·845	1·802
10642	1·141	*Sulphate*	0·028	0·028	0·029	0·029	0·020	0·464
		Pyritic	0·537	0·537	0·546	0·522	0·561	
		Organic	0·579	0·579	0·598	0·598	0·602	0·602
		Total (calc.)	1·144	1·144	1·173	1·140	1·183	1·066
10653*	1·514	*Sulphate*	0·054	0·054	0·060	0·060	0·042	0·683
		Pyritic	0·774	0·771	0·771	0·758	0·790	
		Organic	0·710	0·710	0·730	0·730	0·686	0·686
		Total (calc.)	1·538	1·535	1·561	1·548	1·518	1·369
10660*	3·330	*Sulphate*	0·099	0·099	0·088	0·088	0·100	2·113
		Pyritic	2·375	2·342	2·348	2·374	2·243	
		Organic	0·939	0·939	0·949	0·949	0·843	0·843
		Total (calc.)	3·413	3·380	3·385	3·411	3·186	2·956
10670	1·544	*Sulphate*	0·025	0·025	0·024	0·024	0·027	0·668
		Pyritic	0·692	0·687	0·689	0·692	0·674	
		Organic	0·843	0·843	0·851	0·851	0·778	0·778
		Total (calc.)	1·560	1·555	1·564	1·567	1·479	1·446

Table 4—continued

Table 4—continued

Sample number	Total sulphur (Eschka method)	Form of sulphur	F.R.B. method: 'non-simultaneous' procedure				B.C.R.A. method	
			Iron titrated with mercurous nitrate		Iron titrated with titanous sulphate		Iron titrated with potassium dichromate	
			Pyritic sulphur estimated from Fe per cent	Pyritic sulphur estimated as $BaSO_4$ per cent	Pyritic sulphur estimated from Fe per cent	Pyritic sulphur estimated as $BaSO_4$ per cent	Pyritic sulphur estimated from Fe per cent	Pyritic sulphur estimated as $BaSO_4$ per cent
10671*	1·374	*Sulphate*	0·023	0·023	0·021	0·021	0·017	0·684
		Pyritic	0·692	0·671	0·698	0·675	0·711	
		Organic	0·690	0·690	0·698	0·698	0·649	0·649
		Total (calc.)	1·405	1·384	1·417	1·394	1·377	1·333
10672	4·279	*Sulphate*	0·117	0·117	0·114	0·114	0·094	2·121
		Pyritic	2·590	2·520	2·624	2·569	2·671	
		Organic	1·618	1·618	1·614	1·614	1·584	1·584
		Total (calc.)	4·325	4·255	4·352	4·297	4·349	3·705
10679	2·505	*Sulphate*	0·030	0·030	0·030	0·030	0·006	1·037
		Pyritic	1·170	1·145	1·197	1·178	1·215	
		Organic	1·290	1·290	1·290	1·290	1·270	1·270
		Total (calc.)	2·490	2·465	2·517	2·498	2·491	2·307
10680*	2·435	*Sulphate*	0·224	0·224	0·219	0·219	0·190	1·132
		Pyritic	1·030	1·037	1·042	1·044	1·099	
		Organic	1·174	1·174	1·168	1·168	1·126	1·126
		Total (calc.)	2·428	2·435	2·429	2·431	2·415	2·258

* See footnote to *Table* 2.

by the results obtained for a number of coals of low pyritic iron content examined in the Coal Survey Laboratory, Newcastle. For these coals the simultaneous procedure gave a negative value for pyritic iron, and the sum of the non-pyritic and pyritic iron (as determined by the non-simultaneous procedure) exceeded the value for 'total acid-soluble' iron given by the simultaneous procedure (*Table 5*).

Table 5. Comparison of 'simultaneous' and 'non-simultaneous' extraction of iron

Laboratory number	*Simultaneous method*			*Non-simultaneous method*		
	Total acid-soluble iron (per cent)	*Non-pyritic iron (per cent)*	*Pyritic iron (calc.) (per cent)*	*Non-pyritic iron (per cent)*	*Pyritic iron (per cent)*	*Total iron (calc.) (per cent)*
7955	0·300	0·453	− 0·153	0·456	0·021	0·477
8738F	0·245	0·341	− 0·096	0·335	0·118	0·453
8739	0·203	0·229	− 0·026	0·230	0·046	0·276

Different results by the two procedures were also obtained when the nine selected coals were analysed (see *Table 2*). Four coals (Samples Nos. 10653, 10660, 10671 and 10680) gave results for pyritic sulphur by the 'simultaneous' procedure that are significantly lower than those given by the 'non-simultaneous' procedure. The disagreement was investigated further by carrying out sulphur balances on fresh samples of the coals concerned and on two other coals, and by determining the pyritic sulphur both by precipitation as barium sulphate and by estimation of pyritic iron. The results are shown in *Table 6*; they establish that the value for pyritic sulphur estimated as iron by the 'simultaneous' procedure is erroneously low shown by the fact that using this sulphur value the calculated total sulphur does not agree with the determined total sulphur, whereas when pyritic sulphur is determined as barium sulphate agreement is good. It must therefore be that in these cases some of the non-pyritic iron does not dissolve in nitric acid, so that the 'total acid-soluble' iron is not the sum of the pyritic and non-pyritic iron.

The F.R.B. 'simultaneous' procedure is thus shown to give erroneous results for some coals, and its use should not be continued.

(*d*) *Equivalence of F.R.B. 'non-simultaneous' procedure and the B.S. method*
Like the F.R.B. method the B.S. method also permits simultaneous and non-simultaneous procedures, but the latter has been adopted in this work. Since, however, decomposition of pyrites by nitric acid has been shown to be complete the simultaneous procedure is also permissible since the pyritic sulphur is determined as barium sulphate and not as iron. Comparative results given by the two methods for the nine selected coals are shown in *Table 2*; the agreement is entirely satisfactory.

EXAMINATION OF THE B.C.R.A. METHOD

This method is essentially a modified form of the F.R.B. simultaneous procedure. The hydrochloric acid and nitric acid extractions are carried out at the boiling point and are said to be complete in 30 minutes. There is thus a considerable saving in time and also a probability that the danger of oxidation and solution of pyrites during the hydrochloric acid extraction pointed out by Teichmann (loc. cit.) will be much reduced.

During operation of the method in the Coal Survey, it was noted that for some coals of low rank (e.g. Sample 10660) the nitric acid extract was stained with a brown coloration. The iron precipitate of such an extract was more difficult to filter than normally. and the solution of the precipitate

Table 6. Sulphur balances for coals giving anomalous results

Sample number	*Total sulphur (Eschka method) per cent*	*Form of sulphur*	*F.R.B. method 'Non-simultaneous' procedure*		*F.R.B. method 'Simultaneous' procedure*	
			Pyritic sulphur from iron per cent	*Pyritic sulphur as barium sulphate per cent*	*Pyritic sulphur from iron per cent*	*Pyritic sulphur as barium sulphate per cent*
10653	1·54	*Sulphate*	0·10	0·10	0·10	0·82
		Pyritic	0·70	0·64	0·42	
		*Organic**	0·70	0·70	0·74	0·74
		Total (calc.)	1·50	1·44	1·26	1·56
10660	3·37	*Sulphate*	0·25	0·25	0·25	2·34
		Pyritic	2·16	2·10	2·02	
		*Organic**	0·97	0·97	0·96	0·96
		Total (calc.)	3·38	3·32	3·23	3·30
10666	0·61	*Sulphate*	0·01	0·01	0·01	0·07
		Pyritic	0·07	0·06	(0·002)	
		*Organic**	0·54	0·54	0·55	0·55
		Total (calc.)	0·62	0·61	0·56	0·62
10669	0·48	*Sulphate*	0·01	0·01	0·013	0·05
		Pyritic	0·05	0·04	*Negative*	
		*Organic**	0·42	0·42	0·42	0·42
		Total (calc.)	0·48	0·47	—	0·47
10671	1·34	*Sulphate*	0·04	0·04	0·04	0·66
		Pyritic	0·61	0·55	0·36	
		*Organic**	0·70	0·70	0·69	0·69
		Total (calc.)	1·35	1·29	1·09	1·35
10680	2·44	*Sulphate*	0·30	0·30	0·29	1·19
		Pyritic	0·89	0·89	0·78	
		*Organic**	1·22	1·22	1·22	1·22
		Total (calc.)	2·41	2·41	2·29	2·41

* Eschka determination on residue after nitric acid extraction.

Table 7. Comparison of sulphate sulphur and non-pyritic iron by F.R.B. and B.C.R.A. methods

Sample number	Coalfield	Coal Survey Coal Rank Code No.	Total sulphur per cent	Sulphate sulphur			Non-pyritic iron		
				F.R.B. method (a) per cent	B.C.R.A. method (b) per cent	(a) − (b) per cent	F.R.B. method (c) per cent	B.C.R.A. method (d) per cent	(c) − (d) per cent
10641	Northumberland	602/702	1·91	0·02	0·02	0	0·08	0·07	0·01
10642	Durham	301	1·14	0·03	0·02	0·01	0·07	0·05	0·02
10653	Durham	300	1·51	0·06	0·04	0·02	0·40	0·41	−0·01
10659	N. Derbyshire	702	1·62	0·04	0·03	0·01	0·08	0·05	0·03
10660	S. Derbyshire	902	3·33	0·08	0·10	−0·02	0·46	0·51	−0·05
10662	Cannock Chase	902	4·21	0·15	0·13	0·02	0·26	0·24	0·02
10663	N. Derbyshire	502/602	6·14	0·21	0·15	0·06	0·43	0·34	0·07
10664	Lancashire	902	3·95	0·13	0·15	−0·02	0·38	0·36	0·02
10665	N. Staffordshire	602	2·56	0·04	0·04	0	0·09	0·07	0·02
10666	N. Staffordshire	501	0·61	0·008	0·008	0	1·17	1·17	0
10667	W. Yorkshire	501	1·09	0·004	*Trace*	0	0·03	0·03	0
10668	Lancashire	601	5·10	0·12	0·11	0·01	0·27	0·23	0·04
10669	Lancashire	501	0·46	0·008	0·01	0	1·00	1·00	0
10670	Ayrshire	702	1·54	0·02	0·03	−0·01	0·05	0·05	0
10671	Ayrshire	902	1·37	0·02	0·02	0	0·52	0·52	0
10672	Ayrshire	901	4·28	0·10	0·09	0·01	0·42	0·40	0·02
10673	Warwickshire	902	3·76	0·16	0·17	−0·01	0·28	0·26	0·02
10674	S. Yorkshire	501	1·09	0·04	0·02	0·02	0·08	0·05	0·03
10675	W. Yorkshire	501/601	1·69	0·03	0·02	0·01	0·08	0·08	0
10676	S. Yorkshire	602	1·68	0·02	0·02	0	0·08	0·06	0·02
10677	S. Yorkshire	702	2·89	0·12	0·10	0·02	0·21	0·17	0·04
10678	N. Derbyshire	802	1·59	0·09	0·08	0·01	0·18	0·15	0·03
10679	Durham	401*b*	2·51	0·03	0·006	0·02	0·06	0·02	0·04
10680	Durham	501*b*	2·44	0·21	0·19	0·02	0·34	0·29	0·05
10681	S. Wales	301	0·90	0·02	0·02	0	0·28	0·31	−0·03
10682	S. Wales	202	1·07	0·008	0·01	0	0·17	0·17	0
10683	S. Wales	100	0·76	0·006	0·002	0	0·10	0·09	0·01
16202	N. Derbyshire	702	2·52	0·07	0·03	0·04	0·20	0·15	0·05
16317	Durham	301	2·00	0·06	0·03	0·03	0·23	0·19	0·04
16318	Durham	501*b*	3·98	0·14	0·07	0·07	0·24	0·11	0·13
16319	Durham	300*b*	2·89	0·09	0·04	0·05	0·26	0·16	0·10
Mean difference (F.R.B. method − B.C.R.A. method)						0·011			0·023

retained a brownish tinge after reduction with stannous chloride, making it difficult to judge the completeness of the reduction. It was found that the brown coloration, which is probably due to extracted ulmins, can be destroyed by boiling the extract for 5 minutes with 2 ml of 30 per cent hydrogen peroxide before precipitation of the iron by ammonia.

The results obtained for the nine selected coals by the B.C.R.A. method are given in *Table 2*. Agreement with the B.S. method and the non-simultaneous procedure of the F.R.B. method is generally satisfactory, but there is a definite tendency for the B.C.R.A. method to give slightly lower results for sulphate sulphur and correspondingly higher results for pyritic sulphur. To establish whether or not this is a real difference, a further batch of 31 coals was analysed by the B.C.R.A. and F.R.B. methods and care was taken to ensure that all the analysis was carried out as nearly as possible at the same time to avoid the risk that atmospheric oxidation of the pyrites in the laboratory samples might obscure the issue. The results, given in *Table 7*, confirm the bias noted above; the difference was usually small but in some cases (e.g. Sample 16318) can be appreciable.

The same tendency is seen in the non-pyritic iron results (*Table 7*). For three of the coals where the differences were appreciable the iron contents of the residues from the B.C.R.A. and F.R.B. methods were determined and found to be in good agreement. (*Table 8*)

Table 8. Comparison of residual irons left after F.R.B. and B.C.R.A. extractions

Sample	*Form of iron*	*B.C.R.A. method*	*F.R.B. method*
		Iron (per cent)	*Iron (per cent)*
16202	*Non-pyritic*	0·16	0·19
	Pyritic	1·24	1·21
	Residual	0·12	0·12
	Sum of above	1·52	1·52
	Determined total	1·52	1·52
16318	*Non-pyritic*	0·12	0·22
	Pyritic	2·25	2·18
	Residual	0·11	0·10
	Sum of above	2·48	2·50
	Determined total	2·48	2·48
16319	*Non-pyritic*	0·16	0·24
	Pyritic	1·47	1·40
	Residual	0·06	0·05
	Sum of above	1·69	1·69
	Determined total	1·68	1·68

These data indicate very strongly that the difference between the results is the result of some attack of the pyrites during the prolonged hydrochloric acid extraction used in the F.R.B. and B.S. methods, thus confirming Teichmann's observation.

XUM

It is interesting to note that the B.C.R.A. method did not give low results for pyritic iron, in contrast to the F.R.B. simultaneous procedure. The change in the conditions of the nitric acid extraction appear to have overcome the effect which causes error in the latter method.

This method, modified as below, has now been chosen by the Divisional Analysts' Committee of the National Coal Board as its standard method for the determination of forms of sulphur.

A COLORIMETRIC METHOD FOR THE ESTIMATION OF IRON IN THE F.R.B. AND B.C.R.A. METHODS

In both the above methods pyritic sulphur is determined indirectly by an iron estimation which is carried out volumetrically and which at one stage involves precipitation of the iron. That precipitation being a major potential source of error, it would be an undoubted advantage if the estimation could be carried out by a method that avoids it. Colorimetry suggests itself, and a technique based on a well tried colorimetric method[14] has been found to be satisfactory. The colour is developed with 1,10-phenanthroline in a solution buffered with sodium acetate; the procedure, as used in conjunction with the B.C.R.A. method for extracting the iron from coal, is given in full at the end of this section of the paper.

As a preliminary experiment, twelve 1 g samples of the same coal were extracted with boiling nitric acid by the B.C.R.A. method. Each extract was made up to a known volume and two aliquot parts taken from each for

Table 9. Comparison of colorimetric and dichromate titration results for twelve samples of one coal

Sample	*Amount of iron (per cent)*	
	Colorimetric	*Dichromate titration*
1	1·255	1·260
2	1·239	1·260
3	1·253	1·253
4	1·261	1·260
5	1·260	1·260
6	1·263	1·253
7	1·263	1·267
8	1·260	1·280
9	1·259	1·267
10	1·263	1·253
11	1·263	1·240
12	1·270	1·253
Mean	1·259	1·259
Standard deviation	±0·0076	±0·0095

determination of iron, one by the colorimetric method and the other by titration with potassium dichromate after precipitation and re-solution of the iron. The results are given in *Table 9*.

It is evident that for this coal the two methods agree well and that the colorimetric method gives a slightly smaller spread between replicates.

A second preliminary experiment was carried out to investigate the effect of phosphate ions on the rate of colour development; these ions have been stated[15] to delay development. A coal with 0·1 per cent phosphorus in its ash was chosen and after extraction the phosphorus content of the extract was raised by the addition of sodium di-hydrogen phosphate to the equivalent

Table 10. Effect of phosphorus on colorimetric iron determination: percentage total iron

Phosphorus present (Ash basis : per cent)	0·1	1·1	2·1	3·1
15 *mins*	1·125	1·130	1·130	1·130
1 *hour*	1·125	1·125	1·125	1·125
4 *hours*	1·135	1·135	1·135	1·130
24 *hours*	1·135	1·130	1·135	1·130

of 1·1, 2·1 and 3·1 per cent in the ash. The colours developed were measured at intervals of time up to twenty four hours (*Table 10*).

These results show that the concentrations of phosphates encountered in normal coals have no effect on colour development.

The investigation was then extended to a series of coals of varying rank and sulphur content, with the very satisfactory results given in *Table 11*.

Table 11. Comparison of volumetric and colorimetric methods of iron determination: B.C.R.A. method of extraction

Laboratory	*Coal rank code*	*Form of iron*	*Amount of iron (per cent)*	
			Volumetric	*Colorimetric*
I	502	*Non-pyritic*	1·097	1·115
		Pyritic	2·859	2·885
		Total	3·956	4·000
II	601	*Non-pyritic*	0·138	0·136
		Pyritic	0·558	0·554
		Total	0·696	0·690
III	401	*Non-pyritic*	0·290	0·304
		Pyritic	3·503	3·576
		Total	3·793	3·880
IV	702	*Non-pyritic*	0·066	0·062
		Pyritic	2·068	2·164
		Total	2·134	2·226
V	801	*Non-pyritic*	0·233	0·235
		Pyritic	0·889	0·875
		Total	1·122	1·110
VI	902	*Non-pyritic*	0·039	0·041
		Pyritic	0·316	0·312
		Total	0·355	0·353
VII	201	*Non-pyritic*	0·202	0·205
		Pyritic	0·743	0·693
		Total	0·945	0·898

XUM

Seven Coal Survey Laboratories took part in that investigation and have subsequently analysed a large number of coals by both methods with equally good agreement.

The colorimetric estimation proposed has thus been demonstrated to be reliable and to give results as accurate as those given by the volumetric procedure. In addition to avoiding the possible error involved in iron precipitation, it is appreciably faster than those procedures and has now been adopted as standard practice in the Coal Board.

Procedure

(*a*) *Non-pyritic iron*—Boil 5 g of coal, ground to pass a 72 B.S. mesh sieve, with 50 ml of 5N hydrochloric acid for 30 minutes in a 250 ml conical flask with a 'cold finger' condenser resting in the neck of the flask. Filter the mixture, wash six times with dilute hydrochloric acid using about 20 ml acid in all, and make up to 250 ml with water. Reserve 200 ml of this solution for the gravimetric determination of sulphate sulphur.

Pipette a 2 ml aliquot part of the extract into a 50 ml graduated flask, dilute with approximately 20 ml water, add 5 ml of a 10 per cent aqueous solution of hydroxylamine hydrochloride and a small square of congo red indicator paper. Titrate with 2M sodium acetate solution to the change in colour of the paper (blue to red) and then add 4 ml of a 0·25 per cent aqueous solution of 1, 10-phenanthroline. Make up to volume, allow to stand one hour and measure the extinction in 1 cm cells with light of 5100Å wavelength (filters for Spekker—Ilford 604). Carry out a reagent blank determination at the same time. The colours (which are stable) may be measured either against water or against the blank.

(*b*) *Total acid-soluble iron*—Boil 1 g of coal, ground to pass a 72 B.S. mesh sieve, with 50 ml of 2N nitric acid for 30 minutes in a reflux apparatus of the same form as that used in (*a*). Filter, wash the residue six times with 2N nitric acid and make up the filtrate to 250 ml with water.

Pipette a 5 ml aliquot part into a 50 ml graduated flask and determine the iron as in section (*a*) above.

(*c*) *Calibration*—Prepare a stock Standard Iron solution by dissolving 1·00 g pure iron wire in 100 ml of 1 : 3 nitric acid, boiling to expel oxides of nitrogen, and diluting to 1 litre with water after cooling. Dilute 20 ml of this Stock Standard to 500 ml for a Working Standard Iron Solution. Construct a calibration curve by treating appropriate aliquot parts of the Working Standard Solution (1 to 10 ml at 1 ml intervals) in the manner above to cover the range 40 to 400 μg iron. It is advisable to carry out three determinations at each level and take the average extinction values for the construction of the graph.

Note

When the instrument in use is a spectrophotometer, a straight line calibration graph will be obtained. With the Hilger 'Spekker' absorptiometer, however, although a straight line relationship is still obtained, there is a change of slope above approximately 260 μg iron. The precise point of the change will depend on the characteristics of the individual instrument and the transmission curve of the particular Ilford 604 filter pair used.

CONCLUSIONS

(*1*) The use of B.S. 72-mesh coal for the B.S. and F.R.B. methods is permissible.

(*2*) Mercurous nitrate is a suitable alternative to titanous reagents for the estimation of iron in nitric acid extracts of coal, provided that care is taken to remove oxides of nitrogen before titration.

(*3*) The 'simultaneous' procedure of the F.R.B. method is liable to give erroneous results for pyritic iron.

(*4*) The F.R.B. method ('non-simultaneous' procedure) and the B.S. method give practically identical results, but both are liable to a slight error affecting both sulphate and pyritic sulphur. The B.C.R.A. method is not so subject to oxidation effects and is recommended where the highest accuracy is required.

(*5*) Determination of iron in the F.R.B. and B.C.R.A. methods can be satisfactorily accomplished colorimetrically with 1,10-phenanthroline in acetate-buffered solution. The modification results in increased speed and removes the necessity for an iron precipitation step.

The investigation has been carried out as part of the programme of the Coal Survey, Scientific Department, of the National Coal Board, and the authors acknowledge, with thanks, the permission of the Board to publish the results of the work. They are also indebted to the staff of the Coal Survey Laboratories at Birmingham, Newcastle and Nottingham, and, in particular, to Mr J. K. Hancock who undertook much of the analytical work.

Coal Survey Laboratory,
Newcastle upon Tyne

(*Received May 1957*)

REFERENCES

[1] POWELL, A. R. and PARR, S. W. *Univ. Ill. Bull. No. 111* (1919)
[2] 'Methods for the analysis and testing of coal and coke', *B.S. 1016: 1942*
[3] Fuel Research Board *Survey Paper No. 44*, 'Methods of analysis of coal and coke'. Her Majesty's Stationery Office: London, 1940
[4] POWELL, A. R. *Industr. Engng Chem.* 12 (1920) 887
[5] BUERGER, M. J. *Amer. Min.* 19 (1934) 37
[6] ROUSSEAU, P. E. *BrennstChemie* 12 (1931) 446
[7] TEICHMANN, J. *J. chem. Soc. S. Afr. Bull. No. 22* (1945)
[8] MOTT, R. A. *Fuel, Lond.* 29 (1950) 53
[9] MANTEL, L. W. and RADMACHER, W. *Glückauf* 73 (1937) 989
[10] RADMACHER, W. and MOHRHAUER, P. *Glückauf* 89 (1953) 503
[11] BELCHER, R. and SPOONER, C. E. *Fuel, Lond.* 20 (1941) 172
[12] BRADBURY, F. R. and EDWARDS, E. G. *Chem. & Ind. (Rev.)* 59 (1940) 96
[13] BELCHER, R. and WEST, T. R. *Analyt. chim. Acta* 5 (1951) 268
[14] PRINGLE, W. J. S. *Analyst* 71 (1946) 490
[15] BANDEMER, S. L. and SCHAIBLE, P. *Industr. Engng Chem. (Anal.)* 16 (1944) 317

XUM

Occurrence of Oxides of Nitrogen and Sulphur in the Determination of Carbon and Hydrogen in Coal

R. A. MOTT and H. C. WILKINSON

It is shown that oxides of nitrogen in the gases leaving a Liebig or Sheffield High Temperature combustion tube are negligible in amount and that the acidic gases absorbed in a manganese dioxide absorber after the tube are chiefly oxides of sulphur. The oxides of sulphur from 0·5 g of coal containing up to 2·75 per cent of sulphur can be completely absorbed by the silver spiral in the High Temperature Method, using standard pushing, with the hotter end of the spiral at 860° C; for coals of higher sulphur content 1 per cent of the oxides of sulphur may pass the spiral. Oxides of sulphur may pass the lead chromate packing in the Liebig Method after 40 determinations. A manganese dioxide absorber provides a factor of safety, in that it absorbs acidic gases which may pass the normal packings designed to retain them. The Liebig and Sheffield High Temperature Methods, with manganese dioxide absorbers in the train, give the same mean values of carbon and hydrogen.

TWO methods are to be recommended in the revision of *B.S. 1016* : 1942[1] for the determination of carbon and hydrogen in coal, namely, the Liebig Method (which has been in use in one form or another for over a century) and the Sheffield High Temperature Method, which was devised some 15 years ago by R. BELCHER and C. E. SPOONER[2] and which is likely to displace the older method on the grounds of greater accuracy, speed and convenience. The present authors have reported work on certain features of the latter method[3] and recent work, now to be reported, has further clarified the understanding of the method. L. J. EDGCOMBE[4] has made a comparison of the agreement between, and the repeatability of, the two methods.

THE OCCURRENCE OF OXIDES OF NITROGEN

Much discussion has arisen in recent years regarding the extent to which oxides of nitrogen are produced in the Liebig and the Sheffield High Temperature Methods, it being alleged that these oxides could, in the Liebig Method, give an error of 0·25 per cent of carbon. Since, according to L. J. EDGCOMBE[4], there was no significant difference between the mean percentage carbon for a series of sixteen coals tested by the two methods, and according to A. E. BEET and R. BELCHER[5] no oxides of nitrogen survived in the Sheffield High Temperature Method, it appeared that there was an error in one, at least, of these statements. The present work has resolved this problem.

The error has arisen through proving that certain absorbers will absorb completely oxides of nitrogen from materials likely to yield such oxides (a mixture of benzoic acid, silver nitrate and phenacetin) and then assuming that

the gain in weight of such absorbers when burning coal is due to oxides of nitrogen. As will be shown later, the chief acidic oxides (other than carbon dioxide) which may leave a Liebig or a Sheffield High Temperature combustion tube are oxides of sulphur, not oxides of nitrogen. It is not, therefore, sufficient to base an observation on the increase in weight of a so-called 'oxides of nitrogen absorber': such absorbers should be extracted with water and the nitrate or sulphate determined.

In the Sheffield High Temperature Method for the determination of sulphur and chlorine[6], the hydrogen peroxide will absorb both nitric oxide and nitrogen peroxide. R. BELCHER and G. INGRAM[7] have found pelleted manganese dioxide to be the most convenient solid absorbent for nitrogen peroxide and have recommended its use in an absorber consisting of an inner tube with an annular space outside it to allow for the oxidation of nitric oxide to nitrogen peroxide, the former not being absorbed. Manganese dioxide will, of course, also absorb oxides of sulphur. The use of this absorber in the absorption trains of the Sheffield High Temperature and Liebig Methods for the determination of carbon and hydrogen has been studied and the results of this investigation are reported here.

In the first series of tests, nine coals varying in carbon from 81·9 to 93·3 per cent (dry, mineral-matter-free) were used: the carbon and hydrogen were determined by the Sheffield High Temperature (H.T.) Method, quadruplicate tests being made by the normal procedure, and with a manganese dioxide absorber interposed between the absorbers for water and carbon dioxide. The details of these tests need not be recorded here, it being sufficient to make the following statements. (*1*) There was no observable effect due to rank of coal. (*2*) For seven of the coals, the difference in mean carbon percentage ($C_o - C_w$, where C_o = carbon percentage determined without manganese dioxide absorber and C_w = carbon percentage determined with manganese dioxide absorber) was negative in three cases and the mean (arithmetic) was was only 0·03, approximately equivalent to the mean increase in weight of the manganese dioxide absorber. For seven of the nine coals, therefore, acidic oxides absorbed by the manganese dioxide absorber were negligible in amount. (*3*) The other two coals showed differences in mean carbon percentage ($C_o - C_w$) of over 0·2 and the mean increase in weight of the manganese dioxide absorber (assuming this to be due to nitrogen peroxide) was equivalent to a carbon percentage of the same order. These two coals were both of abnormally high nitrogen content (2·03 and 1·95 per cent, dry, ash-free) and one was of high sulphur (2·22 per cent, d.a.f.).

Coals of high nitrogen, high sulphur; high nitrogen, low sulphur; and low nitrogen, high sulphur were used in further tests in which, after weighing the manganese dioxide absorber, the contents were extracted with very dilute sulphuric acid for 30 min to remove any nitrate. After filtration and oxidation with a little hydrogen peroxide, the solution was evaporated almost to dryness and made up to 100 ml. Each solution was tested for nitrate using phloroglucinol and, if present, the nitrate was determined quantitatively by a colorimetric method using brucine and a Spekker absorptiometer. Duplicate tests were made by both the Liebig and the H.T. Method on each coal, the results being recorded in *Table 1*.

XUM

Remembering the argument previously used by other workers that the gain in weight of a manganese dioxide absorber was due to oxides of nitrogen, it would appear that two 'coals' yielded appreciable quantities of such oxides in the H.T. Method, and one of them also in the Liebig Method. However, the direct determinations of nitrate showed that this argument was untenable, for the quantities of nitrogen peroxide, expressed as equivalent carbon, were negligible for all the coals. It was therefore suspected that the

Table 1. Direct determination of nitrates in, compared with increase in weight of, manganese dioxide absorber

Coal	N	S	*Gain in weight, assumed to be* NO_2*, calculated as equivalent* C *per cent*		*Directly determined nitrate calculated as equivalent* C *per cent*	
	per cent d.a.f.		*H.T. Method*	*Liebig Method*	*H.T. Method*	*Liebig Method*
482	2·09	1·62	0·40	0·20	*Nil*	*Nil*
484	2·22	0·67	0·02	0·07	0·01	0·03
Pyritic fusain	0·42	2·00	0·25	0·07	*Nil*	*Nil*

increase in weight of the manganese dioxide absorber was due to oxides of sulphur and in further tests, using only the Liebig Method, any oxides of sulphur passing the end of the combustion tube (with its lead chromate packing designed to remove such oxides) were absorbed in hydrogen peroxide. The total acidity, now assumed to be sulphur dioxide and calculated as equivalent carbon percentage, was 0·05, 0·05 and nil for the three coals of *Table 1*, respectively, these values being of roughly the same order as those deduced from the gain in weight of the manganese dioxide absorber in *Table 1*.

The conditions under which oxides of sulphur could pass from the end of a combustion tube during the determination of carbon were therefore examined. Since the H.T. Method gave the simplest experimental procedure, this method was used for the first study.

DISCHARGE OF OXIDES OF SULPHUR FROM A HIGH-TEMPERATURE COMBUSTION TUBE

In the first series of tests, four coals of sulphur content (Eschka Method) 0·65, 1·57, 2·79 and 3·82 per cent, d.a.f. (approximately in the ratio 1:2:4:6), were used and the percentage of sulphur recovered by the silver gauze roll was determined for various temperatures of the hotter end of the roll. In these tests, carbon and hydrogen were not determined and the usual absorbers were not used; instead, the acidic gases (other than carbon dioxide) leaving the combustion tube were absorbed in alternate tests in hydrogen peroxide in the single absorber recommended by R. A. MOTT and H. C. WILKINSON[6] for the determination of sulphur, or in a manganese dioxide absorber, duplicate determinations being made by each procedure. The temperatures used were found by making a temperature survey with a thermocouple enclosed in the silver gauze, with the junction just projecting from the gauze, this being slowly pushed into the combustion tube from the exit end, allowed to attain a maximum, pushed in farther, and so on; the temperature

distribution so observed was checked by a similar procedure on withdrawing the thermocouple.

It was found that, with a temperature of 750°C, the oxides of sulphur were never completely removed, even for the low sulphur coal, but at 825°C 100 per cent of the sulphur was removed with the two coals of lower sulphur content but only 83 per cent for the two coals of higher sulphur content; on increasing the temperature to 860°C all the sulphur was retained by the silver roll with the third coal but about one per cent passed with the fourth coal. All these tests were made with 'standard pushing', i.e. six pushes, at intervals of one minute, to the centre of the furnace, where the boat remains for a further four minutes. Further series of tests were made with the time of pushing of the boat to the centre increased to eight, ten, twelve and sixteen minutes, the rate of evolution of gases being thereby reduced. The results of all the tests are recorded in *Table 2*. One further series of tests was made

Table 2. Effect of rate of pushing and maximum temperature of silver gauze on its retention of oxides of sulphur in the H.T. Method for carbon and hydrogen

*Time of pushing (min)**	*Percentage of total sulphur retained by silver gauze at maximum temperatures (°C) of:*									
	750	825	750	825	750	825	860	750	825	860
	Coal 272, S = 0·65		*Coal* 119, S = 1·57		*Coal* 438, S = 2·79			*Coal* 439, S = 3·82		
6	73·8	100·0	54·3	100·0	45·4	82·8	100·0	57·4	82·3	98·9
8	85·2	100·0	76·8	100·0	59·2	96·2	—	49·1	96·5	100·0
10	90·2	100·0	88·7	100·0	59·9	98·1	—	78·3	96·3	—
12	93·5	98·4	95·4	99·9	76·0	98·1	—	—	98·9	—
16	93·5	100·0	94·7	100·0	82·8	97·3	—	88·6	98·9	—

* In every case, the sample was allowed to remain for a further four minutes at 1350°C.

using, at all rates of pushing, instead of the rolled silver gauze, silver chips enclosed between rolls of silver gauze in a silica tube which, with a small clearance, filled the cross section of the combustion tube. This device was tried with a maximum temperature of 750°C; it gave only 40 to 45 per cent absorption of the oxides of sulphur, irrespective of the rate of pushing, and it was concluded that this silver packing was unsuitable.

For the coal of 3·82 per cent sulphur, 100 per cent of the sulphur was retained with a maximum temperature of 860°C and a time of pushing to the centre of eight minutes. For the same temperature, a pushing time of six minutes was sufficient to ensure absorption of all the sulphur from the coal of 2·79 per cent sulphur, and, for this time of pushing to the centre, a temperature of 825°C was sufficient to ensure 100 per cent absorption from the coals of 1·57 and 0·65 per cent sulphur. For the coal of 3·82 per cent sulphur and a maximum temperature of 825°C, the increase in the percentage of sulphur absorbed with a slower rate of pushing to the centre is obvious. It may be concluded, therefore, that, with a temperature of 860°C at the hotter end of the silver gauze roll, at least 99 per cent of the sulphur will be absorbed at the standard rate of pushing for coals containing up to about 3·8 per cent sulphur, this degree of absorption conforming with the recommendations[2] of

XUM

the originators of the test regarding the standardization of the position of the silver roll. Since silver melts at 963°C and silver sulphate decomposes at 923°C, 860°C provides an adequate safety-margin; in practice, the roll could be positioned by determining the temperature with a thermocouple*, instead of by trial to give at least 99 per cent absorption for a coal of 1·5 per cent sulphur.

Thus, if the correct position has been found, some sulphur will pass from the end of the combustion tube, using the standard rate of pushing, only when testing a coal of high sulphur content. Another feature, however, is the efficiency of the silver gauze and, since this decreases with use (as the surface becomes saturated with silver sulphate), a series of tests was made, with the coal of 3·82 per cent sulphur and a time of pushing to the centre of eight minutes, to establish the use permissible before the efficiency falls significantly. The results are recorded in *Table 3*.

Table 3. Efficiency of silver gauze at 860°C in consecutive tests on coal 439; 8 min pushing in hot zone

Test	*Percentage sulphur retained by gauze*	*Test*	*Percentage sulphur retained by gauze*
1	100	5	97·4
2	100	6	97·9
3	100	7	94·5
4	99·6	8	93·0

The effect of saturation of the surface is obvious, but, even with this high sulphur coal, four tests could be made before the retention fell below 99 per cent. Since this corresponds to the absorption of 15·3 per cent of sulphur from 0·5 g of coal, it could be expected that eight or ten tests (a day's work) could be carried out on coals of under 1·5 per cent sulphur without cleaning the gauze.

In the tests recorded in *Table 3* the percentage of sulphur passing the silver gauze was found by direct determination by absorption in hydrogen peroxide and correction for chlorine. As already recorded, two tests were also made for each experimental condition in which the acidic gases were absorbed in the manganese dioxide absorber. The gain in weight of this absorber was measured after each test and the manganese dioxide from each pair of determinations extracted with dilute hydrogen peroxide, the sulphate then being precipitated by the addition of 15 ml of 10 per cent barium chloride solution. In *Table 4* the values obtained for the sulphur, by the various methods of assessment, are recorded, it being assumed that the gain in weight of the manganese dioxide absorber was due to oxides of sulphur: it will be observed that this assumption appears to be justified.

The mean (B—C) for each coal at 750°C or 825°C never exceeds 0·03 and has an algebraic mean of eight values of 0·005, showing that oxides of nitrogen are negligible in amount. The mean (A—B) attains 0·08 for a high sulphur coal at a temperature of 750°C and has an algebraic mean of eight

* On inserting a thermocouple not surrounded by a roll of silver gauze, it was found that a temperature of 910°C corresponded with 860°C with the couple surrounded by the silver gauze.

values of 0·02, suggesting that the efficiency of absorption of acidic gases in the liquid system is rather higher than that in the solid system.

It can be concluded that, in the Sheffield High Temperature Method, oxides of sulphur can be completely absorbed, using the standard rate of pushing, with a hot-end temperature of the silver gauze of 860°C for coals containing

Table 4. Sulphur found in exit gases (H.T. Method) by various methods

Coal	Time of pushing (min)	Sulphur, per cent, by various methods of assessment*								
		750°C			825°C			860°C		
		H_2O_2 (A)	MnO_2 (B)	$BaSO_4$ (C: from B)	H_2O_2 (A)	MnO_2 (B)	$BaSO_4$ (C: from B)	H_2O_2 (A)	MnO_2 (B)	$BaSO_4$ (C: from B)
272	6	0·16	0·16	0·18	*Nil*	*Nil*	*Nil*	—	—	—
	8	0·09	0·10	0·09	*Nil*	*Nil*	*Nil*	—	—	—
	10	0·06	0·05	0·06	*Nil*	*Nil*	*Nil*	—	—	—
	12	0·04	0·05	0·04	0·01	*Nil*	0·02	—	—	—
	16	0·04	0·03	0·04	*Nil*	*Nil*	*Nil*	—	—	—
		Mean A−B nil			*Mean A−B nil*					
		Mean B−C nil			*Mean B−C nil*					
119	6	0·69	0·68	0·66	*Nil*	*Nil*	*Nil*	—	—	—
	8	0·35	0·32	0·34	*Nil*	*Nil*	*Nil*	—	—	—
	10	0·17	0·19	0·20	*Nil*	*Nil*	*Nil*	—	—	—
	12	0·07	0·06	0·07	0·01	*Nil*	*Nil*	—	—	—
	16	0·08	0·07	0·07	*Nil*	*Nil*	*Nil*	—	—	—
		Mean A−B 0·01			*Mean A−B nil*					
		Mean B−C 0·01			*Mean B−C nil*					
438	6	1·43	1·34	1·30	0·45	0·38	0·46	*Nil*	*Nil*	*Nil*
	8	1·07	1·05	1·07	0·10	0·12	0·09	—	—	—
	10	1·05	0·80	0·72	0·05	0·06	0·07	—	—	—
	12	0·63	0·58	0·57	0·05	0·03	*Nil*	—	—	—
	16	0·45	0·47	0·44	0·07	0·08	0·07	—	—	—
		Mean A−B 0·08			*Mean A−B 0·01*					
		Mean B−C 0·03			*Mean B−C −0·01*					
439	6	1·49	1·38	1·40	0·62	0·66	0·64	0·04	—	—
	8	1·78	1·66	1·58	0·15	0·17	0·17	*Nil*	*Nil*	*Nil*
	10	0·76	0·72	0·66	0·16	0·19	0·20	—	—	—
	12	—	—	—	0·04	0·04	0·04	—	—	—
	16	0·47	0·43	0·45	0·04	0·03	0·04	—	—	—
		Mean A−B 0·07			*Mean A−B −0·02*					
		Mean B−C 0·03			*Mean B−C nil*					

* A = acidic gases absorbed by hydrogen peroxide, corrected for chlorine and calculated as percentage of sulphur in the coal.
B = gain in weight of manganese dioxide absorber, assumed to be due to sulphur dioxide and calculated as percentage of sulphur in the coal.
C = sulphur in extract from B, determined by precipitation as barium sulphate and calculated as percentage in the coal.

up to 2·8 per cent sulphur, and that there is 99 per cent absorption for a coal of 3·8 per cent sulphur under the same conditions. It is preferable to absorb the sulphur as completely as possible in the silver gauze, but, for coals of very high sulphur content, small amounts passing the gauze can be absorbed

XUM

in the manganese dioxide absorber. It can also be concluded that the acidic gases absorbed by the manganese dioxide absorber are chiefly oxides of sulphur and that oxides of nitrogen (nitric oxide and nitrogen dioxide) are present only in minute quantities and from coals of exceptionally high nitrogen content: the extent of the presence of these oxides is sufficient to give an error in the carbon percentage, if they are not removed in the manganese dioxide absorber (after oxidation of nitric oxide to nitrogen dioxide), of 0·01 for a coal of 2·2 per cent of nitrogen.

DISCHARGE OF OXIDES OF SULPHUR FROM LIEBIG COMBUSTION TUBE

It is not possible to adjust the conditions in the Liebig Method as in the H.T. Method to obtain a variable discharge of oxides of sulphur. The discharge will obviously depend on the age and degree of saturation of the lead chromate packing used to absorb oxides of sulphur. For example, in determinations using the Liebig Method with the manganese dioxide absorber between the absorbers for water and carbon dioxide, it was observed that the gain in weight of the manganese dioxide absorber increased after 40 determinations (during which the maximum gain in weight was 2·6 mg) to 3·2 mg (41st determination) and 6·2 mg (42nd determination), the packing then being replaced.

It is appropriate to record here a summary of a series of tests, to be discussed later, in which, for ten coals, the carbon and hydrogen were determined in quadruplicate by both the Sheffield High Temperature and the Liebig Methods, using the manganese dioxide absorber in each train. The increase in weight of this absorber was noted and after four tests the absorber was extracted and the sulphur determined by precipitation with excess barium chloride. Assuming the increase in weight to be due to sulphur dioxide, the equivalent sulphur percentage was calculated. The difference between the two estimates was a measure of the oxides of nitrogen. [An increase in weight assumed to be due to sulphur dioxide is twice the equivalent sulphur, and if the (assumed) sulphur dioxide passes to the carbon dioxide absorber and is counted as carbon dioxide, its carbon equivalent is approximately one quarter, so that the equivalent carbon percentage of the residual sulphur is obtained by halving.]

It should be noted that, unlike the previous experience, when a packing had to be discarded after 42 determinations, a packing in one tube was used for 22 determinations and that in another for 12, so that low values of the increase in weight of the manganese dioxide absorber were found.

The actual amounts of sulphur found in the manganese dioxide absorber bore no relationship to the sulphur contents of the coals, except for the coal of 3·8 per cent sulphur by the H.T. Method, for which, since standard pushing was used, the 'slip' of 0·09 per cent sulphur was to be expected. Another point to which attention should be drawn is that three of the coals were of over 2·0 per cent nitrogen (d.a.f.) and three others of over 1·75 per cent nitrogen, so that quite high values for oxides of nitrogen would have been expected if this were at all possible. The mean results for ten coals are recorded in *Table 5.*

It will be observed that the mean sulphur (per cent of coal) determined in the manganese dioxide absorbers is approximately the same in both series of tests, but the mean gain in weight was greater for the Liebig Method, so that the difference is also greater, estimation of the equivalent carbon percentage giving a negligible value (0·01) for the H.T. Method and a value of 0·025

Table 5. Mean increase in weight of, and sulphur present in, manganese dioxide absorbers used in Liebig and H.T. Methods (10 coals in quadruplicate by each method)

Gain in weight calc'd as S(%)		S(%) *determined by extraction*		*Difference*	
Liebig (*A*)	*H.T.* (*C*)	*Liebig* (*B*)	*H.T.* (*D*)	*Liebig* (*A*−*B*)	*H.T.* (*C*−*D*)
0·080	0·054	0·031	0·033	0·049	0·021

for the Liebig Method. M. P. MENDOZA[8] found a mean increase in weight of his manganese dioxide absorber of 1·7 mg per Liebig determination, with a maximum of 2·5 mg, whereas the maximum increases in the tests reported in *Table 5* were 1·9 mg (H.T.) and 1·2 mg (Liebig) and the mean increases 0·5 mg (H.T.) and 0·2 mg (Liebig), showing a more efficient lead chromate packing in the Liebig apparatus than in that used by Mendoza.

It is clear that, in both the Sheffield High Temperature Method and the Liebig Method, the amount of sulphur dioxide passing from the end of the combustion tube can be kept to a low value by the procedure previously advocated, and that the oxides of nitrogen are, in terms of a possible error in carbon, negligible in both tests. The value of the manganese dioxide absorber is that it provides a factor of safety for high-sulphur coals in the H.T. Method and that it indicates, for the Liebig Method, when the lead chromate packing should be renewed.

COMPARISON OF SHEFFIELD HIGH TEMPERATURE AND LIEBIG METHODS

As previously noted, a series of ten coals was used for quadruplicate determinations by both the Sheffield High Temperature Method and the Liebig Method. In the H.T. Method the silver gauze was positioned with the hot end at 860°C, as previously found to be desirable, and standard pushing was used. For the Liebig Method an electric furnace train of the design developed at the Fuel Research Station was used, the combustion tube being packed in accordance with the proposed revision of *B.S. 1016* : 1942 and the maximum temperature of the copper oxide being 820°C. The mean values for each coal by each procedure, and the standard deviations, are recorded in *Table 6.*

Four determinations by the H.T. Method can easily be carried out in a morning but require a whole day on the twin-tube Liebig apparatus. For the first four coals, the whole of the samples were weighed out in the morning and the moisture determined once; subsequently, half the samples were weighed out in the morning and half in the afternoon, two determinations of moisture being made. This probably explains the rather high standard deviations for the first three coals by the Liebig Method.

XUM

The standard deviations for carbon are of the order to be expected in this laboratory for the H.T. Method, but the corresponding values for the Liebig Method are higher than those reported by Edgcombe[4], owing to less familiarity with the method. On the other hand, this is the first occasion on which such a comparison has been made when using the manganese dioxide absorber to prevent an error due to acidic gases, though such errors are comparatively low. The mean differences between the two methods for the ten

Table 6. Comparison of H.T. and Liebig Methods: means of quadruplicate determinations of carbon (C) *and hydrogen* (H), *per cent, d.b.*

Coal	*H.T. Method*				*Liebig Method*				$C_1 - C_2$	$H_1 - H_2$
	Carbon		*Hydrogen*		*Carbon*		*Hydrogen*			
	C_1	σ*	H_1	σ	C_2	σ	H_2	σ		
503	89·87	0·08	2·93	0·05	89·74	0·47	2·95	0·09	0·13	−0·02
506	83·64	0·09	4·95	0·03	83·48	0·52	4·98	0·10	0·16	−0·03
491	83·89	0·07	4·92	0·02	83·73	0·35	4·94	0·02	0·16	−0·02
119	76·37	0·03	4·85	0·05	76·41	0·28	4·90	0·01	−0·04	−0·05
258	81·33	0·10	5·15	0·01	81·05	0·24	5·11	0·06	0·28	0·04
439	76·99	0·16	4·93	0·01	76·94	0·25	4·99	0·10	0·05	−0·06
473	80·83	0·08	5·15	0·02	80·77	0·20	5·18	0·02	0·06	−0·03
306	76·08	0·10	5·06	0·03	76·15	0·09	5·10	0·07	−0·07	−0·04
481	82·20	0·09	5·26	0·04	82·14	0·11	5·27	0·02	0·06	−0·01
484	84·33	0·11	5·23	0·02	84·02	0·36	5·20	0·15	0·31	0·03
σ_m†		$0·09_5$		$0·03_1$		$0·31_6$		$0·07_8$	+0·11‡	−0·02‡
σ_m (ref. 4)		$0·15_1$		$0·04_5$		$0·19_5$		$0·05_4$		

* Standard deviation † Standard deviation of mean ‡ Algebraic mean

coals are not significant in comparison with the standard deviations of the means. It can be concluded, therefore, that both methods, using the manganese dioxide absorber, give the same mean values for carbon and hydrogen, but that the standard deviations in these determinations are higher for the Liebig Method than for the H.T. Method.

The experimental work was carried out by B. Jackson and P. M. Shortland. The work formed part of the programme of the British Coke Research Association, to whom the authors are indebted for permission to publish.

The British Coke Research Association,
74 Grosvenor Street,
London, W.1

(*Received May 1957*)

REFERENCES

[1] 'Methods for the analysis and testing of coal and coke' *B.S. 1016.* British Standards Institution, London, 1942 (Under revision)
[2] BELCHER, R. and SPOONER, C. E. *Fuel, Lond.* 20 (1941) 130
[3] MOTT, R. A. and WILKINSON, H. C. *Fuel, Lond.* 34 (1955) 169
[4] EDGCOMBE, L. J. *Fuel, Lond.* 34 (1955) 185
[5] BEET, A. E. and BELCHER, R. *Fuel, Lond.* 19 (1940) 42
[6] MOTT, R. A. and WILKINSON, H. C. *Fuel, Lond.* 35 (1956) 6
[7] BELCHER, R. and INGRAM, G. *Analyt. chim. Acta* 4 (1950) 118
[8] MENDOZA, M. P. *Document ISO (SFE) 861.* British Standards Institution: London, 1955

The Mineral Matter in Coal I—The Water of Constitution of the Silicate Constituents

J. O'N. MILLOTT

The Coal Survey Organisation of the National Coal Board is making a reassessment of the well known King, Maries and Crossley formula for the calculation of mineral matter in coal from the determined ash and other analytical data. The factor in the formula which, for most coals, has the largest arithmetical effect is that relating to the correction of the determined ash for the water of constitution of the hydrated silicates. The present paper describes the results of a comprehensive investigation of this factor in relation to hand-cleaned, seam samples. The mineral matter from 79 samples of this type, selected to cover the principal coalfields of Great Britain and the range of coal rank, was extracted by a procedure involving very fine grinding. The values for the water of constitution of the hydrated silicates were determined on the extracted material and suitable corrections were applied for the non-silicate materials present. The results show considerable variation. The South Wales anthracites tend to give lower values than other coals, but otherwise there is no apparent relationship with rank. Similarly, although the coals from certain coalfields appear to give values higher, or lower, than the general average no obvious relationship to location is evident. As it is impossible to determine the water of constitution of the silicates in coal samples as a routine it is considered that an average value should be used with stated confidence limits. This value, representing the average of 79 results, is 11·2 per cent, corresponding to a correction factor of 1·13. It is suggested that this factor replaces that previously in use in the King, Maries and Crossley formula and that it should be applied to all British coals irrespective of rank and location. When used for the correction of 'shale' ash to original 'shale' this factor should give, at the 95 per cent level, results which are correct to within ± 0·17 where the 'shale' ash does not exceed 5 per cent and to within ± 0·33 where the 'shale' ash does not exceed 10 per cent.

THE MINERAL MATTER IN COAL

IN STUDYING the properties of coal it is generally necessary to consider these properties in terms of the coal substance, that is of the material free from moisture and mineral matter. Only in this way, for instance, is it possible to make reliable comparisons of their ultimate compositions—carbon, hydrogen and oxygen contents etc. With the increasing attention that is being devoted to coal systematics and to the subject of coal classification it is particularly important that the basis of study should be the substance of the coal and not the coal contaminated with moisture and mineral matter. At one time analytical data were expressed on the dry, ash-free basis as this was considered to reflect sufficiently closely the fundamental properties of the coal, but within recent years this has tended to be less used as reliable formulae for the calculation of mineral matter from the determined ash values have become available.

The calculation of the mineral matter content of a coal from the ash value depends on a knowledge of the changes which occur to the mineral components of the inorganic matter on heating in air. Thus, there is a loss of

water from hydrated silicates, pyrites is converted to ferric oxide etc. The accuracy of the final assessment will obviously depend on the extent to which the assumptions made as regards these changes are valid. That a reliable method for the direct determination of mineral matter content is to be desired in preference to this indirect approach is obvious, but unfortunately such methods of this type as have been suggested in the past have generally proved unsatisfactory.

The present series of papers is concerned with the indirect method for estimating mineral matter and is confined to an examination of the most widely used, and accurate, (KMC) formula for this purpose—that due to J. G. KING, M. B. MARIES and H. E. CROSSLEY[1]. Other and simpler formulae were employed prior to the work of these authors, but whilst their use undoubtedly led to a better means of comparing seam properties than the simple 'dry, ash-free basis', they were obviously of only limited accuracy.

It is considered unnecessary in this paper to review the voluminous literature that has appeared on the general subject of mineral matter in coal, or the papers dealing more specifically with its calculation, as this has been carried out adequately by members of the staff of the B.C.U.R.A. Thus, J. B. NELSON[2] has discussed the minerals associated with coal, and D. FLINT[3] the methods which have been used for estimating mineral matter and the influence of mineral matter in coal classification. Mention should be made, however, of two papers[4, 5] that have appeared subsequently to these reviews. Both of these describe direct methods for the determination of mineral matter and are therefore of special interest. The first of these, due to W. RADMACHER and P. MOHRHAUER[4], has given excellent results on German coals. This method is at present being investigated in relation to British coals. Such results as have been obtained to date have indicated that the method should be of wide application.

The KMC formula

The general formula put forward by King, Maries and Crossley is

$$\text{Mineral matter} = 1{\cdot}09\,A + 0{\cdot}5\,S_{pyr} + 0{\cdot}8\,CO_2 - 1{\cdot}1\,SO_{3,\,ash} + SO_{3,\,coal} + 0{\cdot}5\,Cl$$

where, expressed as percentages of the air-dried coal, A = determined ash, S_{pyr} = pyritic sulphur, CO_2 = carbonate as CO_2, $SO_{3,\,ash}$ = sulphate (SO_3) in ash, $SO_{3,\,coal}$ = original sulphate (SO_3), and Cl = total chlorine. Slight modifications are made to the formula for Scottish and South Wales coals. The assessment of mineral matter by this formula thus requires a considerable amount of analytical data. The application of modern rapid methods has reduced appreciably the time necessary for carrying out some of the determinations, but this disadvantage remains. For this reason the introduction in 1952 of a simpler version by R. L. BROWN, R. L. CALDWELL and F. FEREDAY[6], based on a statistical study of various co-related factors, was particularly opportune. This modification requires only determinations of ash, sulphur and carbon dioxide. It will be appreciated, however, that the accuracy of the simpler version is directly dependent on that of the original expression.

In view of the increased use being made of the KMC formula it was felt that the premises on which certain of the factors are based should be re-examined, and if necessary that these factors should be amended so as to give greater accuracy. One weakness of the method of deriving this formula, and others which have been suggested in the past, is that the values for certain terms were based on mineral matter easily separable from seam samples by hand. Where the composition of this material corresponds fairly closely to that in the finely disseminated condition this is of little consequence, but where it diverges erroneous conclusions can result. With silicate material, for example, there is evidence that the composition of the roof and floor measures and of the easily separable, thick dirt partings differs from that of the fine dirt layers and the finely disseminated material present. In deriving a suitable formula for the calculation of mineral matter it is obviously necessary that the separate terms shall be based on material which is as representative as possible of that present in the seam. From this standpoint it was considered desirable that both the term whereby correction is made for the loss of water of constitution of silicate constituents and that correcting for the loss of carbon dioxide from carbonate minerals should be re-examined. As regards the remaining terms in the formula, that which allows for the conversion of pyrites to ferric oxide on heating ($0{\cdot}5\ S_{pyr}$) appears to be soundly based, as are those which correct for the fixation of sulphur on ashing ($SO_{3,\,coal} - 1{\cdot}1\ SO_{3,\,ash}$)*. The final term, i.e. that allowing for the decomposition of chlorine compounds on heating, is considered to merit re-examination.

The present paper is solely concerned with the term whereby correction is made for the loss of water of constitution from the 'shale' constituents of the mineral matter. With most coals this is the most important part of the KMC formula, especially where the ash content is high. The investigation of the term which allows for the loss of carbon dioxide from carbonate minerals has been completed and will form the subject of a separate paper. The study of the decomposition of chlorine compounds in coal is still in progress.

WATER OF CONSTITUTION OF SILICATE CONSTITUENTS OF MINERAL MATTER IN COAL

A large proportion of the mineral matter associated with coal consists of mineral species belonging to the shale and kaolin groups[2]. Both of these groups of minerals contain combined hydroxyl ions, which give rise to the water of constitution evolved during the standard ashing procedure[7]. S. W. PARR and W. F. WHEELER[8] appear to have been the first to propose multiplying the ash value by a factor to correct for this loss of water of constitution and suggested 1·08. This factor has been studied by other workers and alternatives put forward, notably by A. C. FIELDNER and W. A. SELVIG[9] and the American Society for Testing Materials[10]. King, Maries and Crossley in deriving their formula assumed different values for the water of constitution of the silicate constituents of the mineral matter according to whether the

* Strictly this expression should be $1{\cdot}1\ SO_{3,\,coal} - 1{\cdot}1\ SO_{3,\,ash}$ but as the sulphate in coal is normally very small, King, Maries and Crossley omit the factor 1·1. It is now considered more convenient to express this part of the formula in terms of sulphur, the expression then being 2·8 × sulphate sulphur in coal − 2·8 × sulphur in ash ($2{\cdot}8\ S_{sulph} - 2{\cdot}8\ S_{ash}$).

XUM

coals originated from the English, Scottish or South Wales coalfields. Thus for English coals they proposed a factor of 1·09, for Scottish coals 1·13, and for South Wales coals 1·07. The water of constitution values from which these factors were derived were based on such analyses of clays ('shales') associated with British coals as were available at the time. No mention is made in their paper of the number or nature of the samples concerned, although the coalfield of origin is given. Presumably material from the roofs and floors of seams was considered as well as that from thick dirt partings. The work of R. A. MOTT and R. V. WHEELER[11], and others, as well as considerations of origin, suggest, however, that the compositions of these materials will differ somewhat from those of the very thin dirt layers and finely disseminated mineral particles in the seams. In the work of the Coal Survey Organisation of the National Coal Board most of the coal samples analysed are from pillar sections of seams or borehole cores which have been carefully hand-picked from the thicker dirt partings and from adhering material forming part of the roofs and floors. In this work it is particularly important, therefore, that the assessments of mineral matter shall be based on the characteristics of the inorganic material remaining in the samples and not on those of the material normally removed from samples prior to analysis.

The investigations described were carried out on samples typically prepared as for analysis in Coal Survey work. These samples had been prepared from pillar sections or borehole cores in which all dirt layers more than about $\frac{1}{4}$ to $\frac{1}{2}$ in. in thickness, and all similar layers of inferior coal (ash content exceeding 15 per cent), had been eliminated. Whilst primarily applicable to work on pillar sections and borehole cores, it will be appreciated, however, that the results will have significance in relation to commercial washed grades and perhaps, to a lesser extent, to hand-cleaned commercial grades.

The silicates remaining in the samples prepared in this way include:

(*1*) Those present in the thin layers of dirt and inferior coal not removed by hand-cleaning.

(*2*) Those closely associated with, but not inherent in, the coal substance. This adventitious material probably represents the fine, detrital matter washed or blown into the coal measure swamps at the time of coal formation. This would be intermingled with the decomposing vegetation and later be intimately associated with it on consolidation into coal. It is unlikely that much of this type of material is removed by coal cleaning processes.

(*3*) Those present in the coal cleats etc., representing secondary material introduced into the coal bed by percolating waters after consolidation. Examples are the deposits of kaolinite frequently present in the cleats of seams and impregnating the cavities in fusain.

It would be expected that, as a result of differences in the proportions of the silicate species, there will be small differences in the water of constitution values of each of these categories of material.

Separation of mineral matter

The method used for the determination of the water of constitution of the silicates involved the extraction of the mineral matter from the coal samples by very fine grinding in the presence of paraffin and water. In this method, which is similar to that used by Mott and Wheeler[11], the mineral matter is recovered as an aqueous suspension.

About 100 g of the coal, at 72 B.S. mesh size, was introduced into a Griffin and Tatlock vibratory ball-mill with 75 ml of paraffin and 200 ml of distilled water and ground with stainless steel balls (diameter 0·05 in.) at 1400 rev/min for at least 48 hours. The stainless steel mill had an internal diameter of 5 in. and an overall length of about 6 in. Milling was stopped periodically, the water layer siphoned off and an equal volume of water added. At the end of the run the extracted material was recovered from the aqueous suspension by filtration and the residual coal was similarly recovered from the paraffin layer. Both solids were then washed with benzene until all paraffin was removed. The extracted material was heated in nitrogen for a short time at 110°C to remove the benzene and both this material and the residual coal allowed to attain equilibrium with the atmosphere. A determination of ash content by the standard method was carried out on the residual coal.

Although the period of milling adopted for most of the samples was 48 hours, for some types of coal such as anthracite, heat altered, and certain other coals, it was increased to 72 hours. The amount of material extracted from the different samples, judging from the ash contents of the coals before and after milling, varied considerably and in one or two instances, where the diminution in ash was relatively small, the effect of further milling was examined. Thus, with one sample of coal from the Durham Coalfield (Coal Rank Code 301b) the ash value had only been reduced from 7·8 per cent to 6·6 per cent on milling for 72 hours. On returning the residual coal to the mill for a further period of 70 hours the additional amount of material extracted, after allowing for the increased amount of attrition products from the mill itself, was only 0·2 per cent. Again, with a sample of the Cornish Four Feet Seam from South Wales (Coal Rank Code 102), with an ash content of 6·1 per cent, the difference in ash content of the residual coal on milling one portion for 72 hours and another for 120 hours was 0·6 per cent. From these and similar tests made on other samples it was concluded that extending the period of milling was unlikely to increase materially the amount of mineral matter extracted. Further extension of this period, too, would have the disadvantage that the amount of attrition products would be increased. Coals in which the diminution of ash content on milling was relatively small presumably contain a high content of either inherent mineral matter or finely disseminated adventitious mineral matter or, of course, both.

The following determinations were made on each sample of the extracted materials:

(*1*) Water evolved at 110°C (hygroscopic moisture).

(*2*) Carbon dioxide content to permit calculation of the amount of carbonate minerals present. In these investigations a value of 2·31 for the ratio

XUM

of carbonate mineral/carbon dioxide was adopted for all samples following recent investigation on the average composition of these minerals based on samples from all the principal British coalfields*. This value is substantially the same as that (2·29) quoted by King, Maries and Crossley in their paper for 'ankerite' from coals other than those from South Wales, but differs from the value (2·46) they gave for South Wales 'brass-stone'.

(*3*) Pyritic sulphur in order to calculate the amount of pyrites, using the factor $1{\cdot}875 \times S_{pyr}$.

(*4*) Total carbon in order to correct for the amount of organic carbonaceous matter present.

The water of constitution was then determined by carrying out a Liebig combustion determination, making an allowance for the water due to combustion of the hydrogen in the carbonaceous matter. The total weight of extracted material from each sample, less the weights of hygroscopic water, pyrites, carbonate minerals and carbonaceous matter present, gave the weight of silicate matter plus attrition products from the mill. It was found that a small correction was generally necessary for the latter. The grinding pot, being made of austenitic stainless steel, showed negligible wear, but the case-hardened steel balls showed signs of attrition. An analysis of the steel of which the balls were made showed that they contained 13·7 per cent of chromium and 0·69 per cent of nickel. By determining, colorimetrically, the chromium content of samples of the extracted material the equivalent weight of steel was calculated and allowance made.

The scheme of correcting for the weights of non-silicate material in the extracted matter by determinations of the amounts of carbon dioxide, pyritic sulphur, organic carbon and chromium and applying factors has the disadvantage that its reliability is directly dependent on the accuracy of these factors. The factor for correcting pyritic sulphur to pyrites is probably reliable, but that for carbonate minerals from carbon dioxide, being based on average values, may lead to a small error. The assumption is also made that the carbonaceous matter in the extracted material has the same composition as the original coal. Where the various corrections are small any inaccuracies of this type will have very little effect on the final values for water of constitution, but they may be significant if the corrections are excessive. An attempt to reduce the values of certain of the corrections by removal of part of the non-silicate constituents directly from the extracted material by flotation was unsuccessful. Samples of this material were floated on bromoform (specific gravity 2·29) and the suspension centrifuged. Where the amounts of pyrites were small it was found that only part of the pyrites (specific gravity 4·8 to 5·1) was removed; where, on the other hand, pyrites constituted about 30 per cent, the portion sinking in the bromoform contained considerable amounts of silicates.

Preliminary tests

Before the actual water of constitution determinations were made on the selected series of coal samples, preliminary tests were carried out on certain aspects of the techniques it was proposed to use.

* An account of the investigations on which this factor is based forms Part II of this series of papers.

(*1*) *Hydration test*—Whilst it is unlikely that the procedure for extracting the mineral matter from coal would lead to hydration, or further hydration, of the silicates present it was thought advisable to test this. A sample of shale from the roof measures of a seam was taken and ground to 72 B.S. mesh size. On one portion of the material milling was carried out in the presence of paraffin and water as for coal samples. On the other part of the material milling was performed in the presence of paraffin only. Water of constitution determinations were then made on each part. In the absence of water the water of constitution value was 6·8 per cent and in the presence of water it was 7·0 per cent. It was considered that this represents satisfactory agreement. Assuming the silicates in the roof 'shale' are similar in composition (though in different proportions) to those in coal samples it is reasonable to conclude that no further hydration occurs in the mineral matter in the course of extraction and analysis.

(*2*) *Behaviour of mineral matter*—An investigation was made to see how, in a coal sample, the water of constitution value for the mineral matter in the portion of the sample floating at 1·6 specific gravity compared with that which sinks at this specific gravity. A sample of the Trencherbone Seam, at 72 B.S. mesh size, from the Lancashire Coalfield was floated at 1·6 specific gravity using carbon tetrachloride and the water of constitution values obtained separately for the floats and sinks fractions; the results are shown in *Table 1*.

Table 1. Extracted material from the Trencherbone Seam

Sample	*Ash in sample before milling* %	*Ash in sample after milling* %	*Material extracted on milling*							*Water of of constitution % of silicates* $\frac{a}{a+b}$
			Pyrites (calc.) %	*Carbonate minerals (calc.)* %	*Carbonaceous material (calc.)* %	*Contaminating steel* %	*Hygroscopic water* %	*Water of constitution* % (*a*)	*Silicates less water of constitution (by diff.)* % (*b*)	
Floats at 1·6 sp.gr.	4·4	2·2	0·2	<0·1	2·4	3·9	5·1	10·6	77·7	12·0
Sinks at 1·6 sp.gr.	47·2	—	22·3	2·2	27·1	2·6	2·3	5·3	38·2	12·2

The water of constitution values for the floats and sinks fractions are similar but it must be borne in mind that the value for the sinks fraction can only be accepted as approximate in view of the excessive corrections that had to be applied. The silicates extracted from the sinks fraction will be mainly those present in the thinner dirt layers remaining in the samples. Those extracted from the floats presumably will be mainly silicate matter which, although strictly adventitious, is closely associated with the coal substance. There will undoubtedly be present also some entrained material which would otherwise sink as experience has shown that it is difficult to avoid this entrainment when carrying out flotation tests on fine coal. Within the limitations of the test, however, it is interesting to note that the water of constitution values for the silicates present in the floats and sinks fractions are similar.

XUM

Table 2. Water of constitution of silicate constituents in British coals. The samples are arranged in order of increasing water of constitution values within Coal Rank Code groups

Coalfield	Colliery or borehole	Seam	Original coal			Ash in coal after milling %	Material extracted on milling							Water of constitution (% of silicates) $\frac{100a}{a+b}$	Factor $\frac{a+b}{b}$	Average water of constitution (% of silicates) for each Coal Rank Code group	Average factor for each Coal Rank Code group
			Coal Rank Code	VM (d.m.m.f.) %	Ash %		Pyrites (calc.) %	Carbonate minerals (calc.) %	Carbonaceous matter (calc.) %	Contaminating steel %	Hygroscopic water %	Water of constitution % (a)	Silicates less water of constitution (by diff.) % (b)				
Fifeshire	*Michael*	*Branxton*	802/902	40·3	4·1	0·9	5·6	11·0	1·6	4·9	1·9	7·9	67·1	10·5	1·12		
Warwickshire	*N. Warwick*	*High Main*	902	39·3	2·4	1·1	13·7	5·2	2·7	2·2	3·9	7·9	64·4	10·9	1·12		
Lothians	*Newcraighall*	*Four Foot*	802/902	40·1	6·7	1·9	1·5	4·7	1·3	1·8	1·7	9·9	79·1	11·1	1·13		
Notts. and N. Derbyshire	*Bestwood*	*High Main*	902	40·4	7·8	2·0	0·6	8·2	0·8	3·2	1·6	9·7	75·9	11·3	1·13		
Notts. and N. Derbyshire	*Hucknall*	*High Main*	902	42·2	5·9	1·2	1·1	9·8	1·7	6·4	2·1	9·2	69·7	11·7	1·13	11·8	1·13
Warwickshire	*Arley*	*Ryder*	802/902	36·1	6·8	1·5	5·3	27·7	1·8	0·4	1·6	7·5	55·7	11·9	1·13		
Fifeshire	*Frances*	*Lethamwell*	902	37·5	7·0	1·3	4·2	13·9	1·3	5·1	1·9	8·8	64·8	12·0	1·14		
Lothians	*Fleets*	*Four Foot*	902	39·3	5·7	1·5	3·8	0·4	1·8	3·0	2·3	11·0	77·7	12·4	1·14		
Lancashire	*A1/1 borehole*	*Worsley Four Foot*	902	37·4	6·3	2·0	12·7	3·7	1·9	4·0	3·2	9·3	65·2	12·5	1·14		
Lothians	*Newcraighall*	*Salters*	802/902	39·4	6·5	1·2	4·3	8·4	1·3	4·9	1·6	10·0	69·5	12·6	1·14		
Lothians	*Easthouses*	*Great*	901	33·9	5·6	1·5	0·8	6·2	1·0	2·0	1·6	11·3	77·1	12·8	1·15		
Notts. and N. Derbyshire	*Ollerton*	*Top Hard*	801	33·7	9·7	1·8	2·4	1·5	0·8	2·8	3·8	9·3	79·4	10·5	1·12		
Yorkshire	*Fryston*	*Flookton Thick*	802	37·7	6·0	2·1	6·7	0·4	1·3	5·8	2·5	8·9	74·4	10·7	1·12		
Warwickshire	*Griff Clara*	*Seven Feet*	802	41·8	3·7	1·9	14·8	1·2	4·3	2·2	1·4	8·6	67·5	11·3	1·13		
Ayrshire	*Mauchline*	*Hurlford Main*	802	39·0	8·2	2·8	10·3	0·1	1·6	1·7	2·0	9·6	74·7	11·4	1·13		
Northumberland	*Ulgham Grange No. 17/41 borehole*	*Plessey*	802	37·5	7·6	1·8	5·0	1·1	0·7	0·6	1·1	10·5	81·0	11·5	1·13	11·7	1·13
Yorkshire	*Highgate*	*Cudworth*	802	39·9	7·1	1·0	1·1	0·5	2·0	15·5	10·0	8·2	62·7	11·6	1·13		
Lothians	*Dalkeith*	*Barrs*	802	41·7	5·2	1·6	1·1	4·0	1·1	6·8	3·0	10·0	74·0	11·9	1·14		
Lothians	*Gilmerton*	*Perpetual*	802	36·3	5·2	1·3	0·4	0·1	1·5	5·6	3·0	10·9	78·5	12·2	1·14		
Warwickshire	*North Warwick*	*Double*	802	40·4	5·1	1·9	28·8	2·7	6·6	3·7	2·9	7·0	48·3	12·7	1·14		
Lothians	*Ramsay*	*South*	801	35·0	5·4	1·6	0·4	0·1	1·8	7·4	3·2	11·4	75·7	13·1	1·15		
Lancashire	*Cronton*	*Crombouke*	702	37·6	5·5	2·4	20·6	27·7	1·7	2·9	2·7	4·7	39·7	10·6	1·12		
Lancashire	*Ellerbeck*	*Trencherbone*	702	37·6	8·9	4·1	11·0	1·8	9·1	1·9	3·0	7·8	65·4	10·7	1·12		
Scottish Central	*Kingshill No. 2*	*Woodmuir Smithy*	702	36·6	7·4	1·8	1·0	0·9	0·8	2·6	1·2	10·2	83·3	10·9	1·12		
Notts. and N. Derbyshire	*Babworth borehole*	*Seam at 2108 ft*	702	41·1	7·2	1·5	1·6	7·1	0·9	2·2	2·5	9·5	76·2	11·1	1·12		
Yorkshire	*Manton*	*Barnsley*	701	35·3	5·6	1·1	0·2	14·9	0·8	1·4	1·8	9·3	71·6	11·5	1·13		
Lancashire	*Bradford*	*Radley*	602/702	38·2	8·1	3·3	2·6	10·0	2·5	2·0	2·1	9·3	71·5	11·5	1·13	11·9	1·13
Scottish Central	*Northfield*	*Armadale Main*	702	36·2	7·8	1·5	0·7	0·3	0·8	1·6	1·4	11·1	84·1	11·7	1·13		
Dumfriesshire	*Fauldhead*	*Creepie*	702	38·5	4·9	1·9	17·7	3·5	1·4	2·8	1·6	8·9	64·1	12·2	1·14		
Dumfriesshire	*Fauldhead*	*Splint*	702	38·1	5·2	1·8	1·5	1·4	1·2	0·8	1·1	11·6	82·4	12·3	1·14		
North Wales	*Ifton*	*Main*	702	40·0	6·8	3·8	16·5	4·4	3·6	3·1	3·4	9·4	59·6	13·6	1·16		
Lancashire	*Cronton*	*Trencherbone*	701	34·4	8·4	3·0	8·6	31·3	0·2	1·5	0·9	8·4	49·1	14·6	1·17		
Northumberland	*Cambois No. 72 borehole*	*Top Plessey*	602	38·2	4·4	1·8	2·1	0·5	1·0	1·8	2·1	8·8	83·7	9·5	1·11		
Lancashire	*A1/1 borehole*	*Seam at*	[illegible]														
Dumfriesshire	*Fauldhead*	*Twenty Inch*	602	41·7	4·8	1·9	16·3	21·2	0·7	1·4	1·2	7·0	76·2	11·8	1·14		
Lancashire	*A3/3 borehole*	*Yard*	601	34·3	7·1	3·1	2·3	6·3	2·4	0·4	1·2	11·0	76·4	12·8	1·15		
Scottish Central	*Kingshill No. 1*	*Wilsontown Main*	602	39·5	6·8	2·4	0·1	0·2	0·8	2·7	2·8	12·0	81·4	12·8	1·15		
Yorkshire	*Dinnington*	*Barnsley*	601	35·4	5·2	1·8	13·6	2·9	1·3	4·7	2·1	10·5	64·9	13·9	1·16		
Northumberland	*Woolsington No. 15 borehole*	*Brockwell*	502	39·2	9·2	2·2	3·6	0·2	0·9	4·8	1·7	7·6	81·2	8·6	1·09		
Northumberland	*North Seaton No. 162*	*Victoria of Choppington*	502	38·5	6·7	1·0	3·6	5·4	1·6	2·6	2·1	8·0	76·7	9·4	1·10		
Yorkshire	*Brookhouse*	*Thorncliffe*	501	36·0	5·6	2·3	13·9	10·2	2·6	6·0	2·9	6·4	58·0	9·9	1·11		
Yorkshire	*South Kirkby*	*Dunsil*	502	38·9	7·4	2·5	10·4	1·8	3·0	2·4	3·4	7·9	71·1	10·0	1·11	10·7	1·12

Lancashire	*No. 72 borehole A1|1 borehole*	*Top Plessey Seams &c.*	602	38·2	4·4	1·8	2·1	0·5	1·0	1·8	2·1	8·8	83·7	9·5	1·11		
Dumfriesshire	*Fouldhead*	*Twenty Inch*	601	37·9	7·3	3·4	10·6	2·5	2·4	4·4	2·3	11·0	76·4	12·6	1·14		
Lancashire	*A3|3 borehole*	*Yard*	601	34·3	7·1	3·1	2·3	6·3	2·4	0·4	1·2	11·0	76·4	12·6	1·14		
Scottish Central	*Kingshill No. 1*	*Wilsontown Main*	602	39·5	6·8	2·4	0·1	0·2	0·8	2·7	2·8	12·0	81·4	12·8	1·15		
Yorkshire	*Dinnington*	*Barnsley*	601	35·4	5·2	1·8	13·6	2·9	1·3	4·7	2·1	10·5	64·9	13·9	1·16		
Northumberland	*Woolsington No. 15 borehole*	*Brockwell*	502	39·2	9·2	2·2	3·6	0·2	0·9	4·8	1·7	7·6	81·2	8·6	1·09		
Northumberland	*North Seaton No. 162*	*Victoria of Choppington*	502	38·5	6·7	1·0	3·6	5·4	1·6	2·6	2·1	8·0	76·7	9·4	1·10		
Yorkshire	*Brookhouse*	*Thorncliffe*	501	36·0	5·6	2·3	13·9	10·2	2·6	6·0	2·9	6·4	58·0	9·9	1·11		
Yorkshire	*South Kirkby*	*Dunsil*	502	38·9	7·4	2·5	10·4	1·8	3·0	2·4	3·4	7·9	71·1	10·0	1·11		
North Wales	*Llay Main*	*Queen*	402/502	36·6	4·8	2·7	14·7	10·1	2·3	1·9	2·2	7·0	61·8	10·2	1·11	10·7	1·12
Notts. and N. Derbyshire	*Westhorpe 50's Level*	*Deep Hard*	502	38·2	9·8	2·7	3·2	14·2	3·8	1·8	2·1	7·9	67·0	10·5	1·12		
North Wales	*Llay Main*	*Stone*	501	35·3	6·9	3·8	13·3	3·3	4·9	4·0	2·5	7·7	64·3	10·7	1·12		
Durham	*Ravensworth Park*	*Six Quarter*	501	32·7	6·9	3·9	1·4	4·7	6·6	2·8	2·5	9·5	72·5	11·6	1·13		
Lancashire	*A1|1 borehole*	*Trencherbone*	501	34·3	5·9	2·5	20·0	3·0	5·5	2·5	2·1	8·6	58·3	12·9	1·15		
Scottish Central	*Kingshill No. 1*	*Wilsontown Main*	502	38·9	5·5	1·7	0·1	0·2	0·8	3·6	3·2	12·2	79·9	13·2	1·15		
Yorkshire	*Wombwell*	*Top Fenton*	402	36·3	5·3	3·2	5·8	14·5	1·9	6·8	3·7	6·6	60·7	9·8	1·11		
North Staffs.	*Holditch*	*Five Feet*	401	33·7	6·5	2·7	11·8	31·2	1·8	3·5	3·2	5·1	43·4	10·5	1·12		
Northumberland	*Annitsford borehole*	*Bandy of Morpeth*	402	41·0	6·1	1·8	0·5	0·2	2·0	2·8	1·5	11·3	81·7	12·2	1·14	11·2	1·13
Lancashire	*Mosley Common*	*Pasture*	402	36·1	6·6	3·3	1·9	21·0	2·4	2·0	1·9	8·8	62·0	12·4	1·14		
Durham	*Pit House*	*Mixed Seams*	301*b*	28·3	7·8	6·6	10·6	11·5	3·8	5·7	5·4	5·4	57·6	8·6	1·09		
Lancashire	*Hoddlesden*	*Lower Mountain*	301*b*	31·8	6·5	1·6	1·8	14·6	2·3	2·5	2·6	7·8	68·4	10·2	1·11		
Durham	*West Thornley Drift*	*Harvey*	301*b*	29·1	5·8	4·0	0·4	0·1	2·1	9·7	4·3	8·6	74·8	10·3	1·11		
Lancashire	*Nabb*	*Union*	301*b*	29·0	8·2	6·8	0·6	1·3	3·4	5·4	5·7	8·9	74·7	10·6	1·12		
South Wales	*Cwm*	*Lower Two Feet Nine*	301*a*	24·6	6·7	3·9	0·6	33·3	3·5	1·3	2·3	6·9	52·1	11·7	1·13	11·0	1·12
Kent	*Snowdown*	*Millyard*	301*a*	19·7	5·6	3·2	8·4	12·5	1·3	10·4	4·9	7·3	55·2	11·7	1·13		
South Wales	*Nine Mile Point*	*Lower Black Vein*	301*b*	30·1	8·8	4·2	0·8	7·4	2·9	4·8	2·2	10·1	71·8	12·3	1·14		
Scottish Central	*Plean*	*Twenty Inch*	301*b*	31·1	5·3	2·6	0·5	6·0	2·8	0·8	1·6	11·4	76·9	12·9	1·15		
South Wales	*Ogilvie*	*Lower Four Feet*	201	13·2	4·9	2·9	9·1	5·5	4·2	6·5	5·8	8·0	60·9	11·6	1·13		
South Wales	*Deep Navigation*	*Four Feet*	202	14·9	4·8	2·8	0·1	9·9	3·0	4·2	2·9	7·6	72·3	9·5	1·11		
South Wales	*Ogilvie*	*Seven Feet*	202	13·6	6·9	3·0	1·7	7·9	3·0	5·0	2·8	8·3	71·3	10·4	1·12		
South Wales	*Park*	*Two Feet Nine*	203	16·2	6·7	3·4	0·2	10·8	5·3	1·0	2·7	9·0	71·0	11·2	1·13	11·0	1·13
South Wales	*Tymawr*	*Upper Five Feet*	203	15·9	5·1	2·9	0·5	6·8	6·4	3·2	2·1	9·8	71·2	12·1	1·14		
South Wales	*Tymawr*	*Six Feet*	204	18·6	6·8	4·0	0·9	17·6	3·6	1·8	2·2	7·3	66·6	9·9	1·11		
Kent	*Betteshanger*	*'F'*	204	17·1	7·5	2·9	0·6	0·6	4·2	2·6	5·4	10·5	76·1	12·1	1·14		
South Wales	*New Cross Hands*	*Big Vein*	101	5·8	4·9	0·8	0·3	3·6	6·7	2·5	3·9	6·7	76·3	8·1	1·09		
South Wales	*Gwaun-cae-Gurwen*	*Lower Vein*	101	5·4	7·5	2·1	0·3	4·2	3·5	5·4	3·1	7·1	76·4	8·5	1·09		
South Wales	*Blaenhirwaun*	*Lower Pumpquart*	101	4·9	4·4	1·5	0·5	14·1	3·7	2·7	2·8	7·6	68·6	10·0	1·11		
South Wales	*Carway*	*Ddugaled*	101	5·8	7·3	2·0	0·8	13·1	3·6	2·3	2·6	8·2	69·4	10·6	1·12		
South Wales	*Cefn Coed*	*White Four Feet*	102	6·7	8·6	2·9	0·8	4·6	5·1	1·0	2·7	7·7	78·1	9·0	1·10	9·5	1·10
South Wales	*Aberpergwm*	*White Four Feet*	102	7·1	5·9	1·6	0·5	10·0	2·9	4·1	2·5	7·5	72·5	9·4	1·10		
South Wales	*Onllwyn No. 1*	*Cornish Four Feet*	102	6·7	6·1	4·2	1·6	7·2	4·9	3·4	1·1	8·0	73·3	9·8	1·11		
South Wales	*Pwllbach*	*Red Vein*	102	6·4	6·0	1·7	0·9	11·6	3·0	2·6	3·8	8·1	70·0	10·4	1·12		
Heat altered coals																	
Scottish Central	*Gartshore 3|12*	*Meiklehill Wee*	306	21·4	4·3	2·3	2·5	1·7	4·0	4·8	2·2	8·0	76·8	9·4	1·10		
Scottish Central	*Ardenrigg*	*Upper Drumgray*	102	6·7	9·2	1·8	0·6	2·3	4·2	13·6	2·8	7·5	69·0	9·8	1·11		
Scottish Central	*Gartshore 3|12*	*Meiklehill Wee*	206	15·2	6·5	4·0	1·8	1·8	4·1	4·3	2·6	9·2	76·2	10·8	1·12		

Determinations of water of constitution of silicates in selected coal samples
The determinations were made on 79 samples covering all the principal coalfields of Great Britain and most of the ranks of coal available in these coalfields. The samples were supplied by the various Coal Survey Laboratories, mostly from reference material which had been obtained in the course of routine investigations on pillar sections and borehole cores and stored in air-tight containers. In order that the amounts of material extracted on milling should be adequate for examination and that the corrections for carbonate minerals and pyrites in this material would be within reasonable limits the samples were selected so that the ash contents were not less than 4 to 5 per cent and the carbon dioxide and sulphur contents as low as possible. This selection in some coalfields proved difficult and in a number of instances it was necessary to use samples with carbon dioxide contents up to 0·5 or 0·6 per cent and sulphur contents up to 2 per cent. Where the ash contents were not less than about 8 per cent samples having these upper limits were, however, regarded as acceptable. The samples were from unweathered material.

The constituents of the materials extracted from the various samples are shown in *Table 2* with the values for the water of constitution of the silicates present and the factors for converting 'shale' ash to original 'shale' based on them; the samples are grouped by Coal Rank Code and average values are given for the groups. *Table 3* gives the values for the water of constitution and the corresponding factors for the samples grouped by coalfields.

In using the data shown in *Tables 2* and *3* for the correction of 'shale' ash to original 'shale' the assumption is made that the water of constitution values of the silicates remaining in the samples after milling are similar to those of the silicates in the extracted matter. The extent to which this is valid is uncertain. A considerable part of the residual silicates will be in the form of finely dispersed material, closely associated with the coal substance, which it is difficult, or impossible, to extract completely by grinding procedures. The water of constitution of this adventitious material may be assumed to approximate to that of the portion extracted. The remainder of the mineral matter will be mainly that present in the original vegetation. Some of this inherent mineral matter may well contain water of constitution but the amount is unknown. In the absence of this information and a knowledge of the actual quantities of inherent matter in the samples it is considered advisable to assume that the values for water of constitution of the silicates in the residual and extracted matter are the same.

Discussion of results
The following facts emerge from a study of *Tables 2* and *3*.

(*1*) Irrespective of type of coal and coalfield or origin most of the samples give values for water of constitution and the corresponding factor that are higher than those used by King, Maries and Crossley in deriving their formula.

(*2*) For coals having the Coal Rank Codes 200 to 900 there appears to be no obvious relation between these values and coal rank.

(*3*) The average values for the samples of South Wales anthracite (Coal Rank Codes 101 and 102) are lower than those for any other group of samples.

(*4*) The available information for South Wales Coals other than anthracite does not indicate that the values are significantly different from those of

Table 3. Values for water of constitution of silicate constituents of British coals, arranged by coalfields

Coalfield	*No. of samples*	*Coal Rank Code range*	*Water of constitution of silicates, %*		*Original 'Shale' Factor* ——— *'Shale' ash*	
			Range	*Average*	*Range*	*Average*
All coalfields	79	100–900	8·1–14·6	11·2	1·09–1·17	1·13
England and Wales except S. Wales anthracite	50	200–900	8·6–14·6	11·1	1·09–1·17	1·13
Scotland	21	100–300 & 500–900	9·4–13·2	11·8	1·10–1·15	1·13
Northumberland and Durham	8	300–800	8·6–12·2	10·2	1·09–1·14	1·11
Yorkshire	8	400–800	9·8–13·9	11·0	1·11–1·16	1·12
Lancashire	11	300–700 & 900	9·6–14·6	11·7	1·11–1·17	1·13
North Wales	3	400/500, 500 & 700	10·2–13·6	11·5	1·11–1·16	1·13
Nottinghamshire and N. Derbyshire	5	500 & 700–900	10·5–11·7	11·0	1·12–1·13	1·12
N. Staffordshire	1	400	10·5	10·5	1·12	1·12
Warwickshire	4	800 & 900	10·9–12·7	11·7	1·12–1·14	1·13
S. Wales (steam and bituminous)	8	200 & 300	9·5–12·3	11·1	1·11–1·14	1·13
S. Wales (anthracite)	8	100	8·1–10·6	9·5	1·09–1·12	1·10
Kent	2	200 & 300	11·7 & 12·1	11·9	1·13 & 1·14	1·14
Scotland—Fifeshire	2	800/900 & 900	10·5 & 12·0	11·2	1·12 & 1·14	1·13
Scotland—Lothians	7	800 & 900	11·1–13·1	12·3	1·13–1·15	1·14
Scotland—Central	8	100–300 & 500–700	9·4–13·2	11·4	1·10–1·15	1·13
Scotland—Dumfriesshire	3	600 & 700	11·8–12·3	12·1	1·13–1·14	1·14
Scotland—Ayrshire	1	800	11·4	11·4	1·13	1·13

most English coals. There seems no justification, therefore, for grouping all South Wales coals together and assuming a different factor as did King, Maries and Crossley.

(*5*) Both the average water of constitution value and the corresponding factor for the samples from the Northumberland and Durham coalfields are lower than those given by the samples from South Wales (excepting anthracite) and all other British coalfields.

(*6*) The average water of constitution value for the Scottish samples is somewhat higher than for the English and Welsh samples other than anthracite, but the individual values fall within the range for England and Wales and the average value of the factor is the same.

XUM

(7) Information is available for only three samples of heat-altered coals. The water of constitution values and the corresponding factors for the two coals of lowest volatile matter and presumably, therefore, the most affected by thermal influences, fall within the range of those for English and Welsh coals other than anthracite, the average value, however, being somewhat lower.

Revision of factor to correct for loss of water of constitution

An examination of the average values of the factors for converting 'shale' ash to original 'shale' for the various groupings of coals shown in *Table 3* suggests there is little justification for using a value other than the general average of 1·13 for any one group. Consideration has been given as to whether a separate factor of 1·11 for South Wales anthracite and the low volatile, heat-altered coals would be justified and also as to whether certain regional factors should be adopted. Thus it might be considered that for Northumberland and Durham coals a factor of 1·11 would be applicable and for Scottish coals, other than the heat-altered types, one of 1·14. The wide spread of the individual values within any one group does not, however, seem to warrant this. Further, before the use of separate factors could be justified for any one class of coal, or for different regions, it would be necessary to examine a much larger number of samples within each group than has been possible in the present investigations.

A mean value for the factor of 1·13 results whether it is obtained by simply averaging the values for all 79 samples or, in order to give the same weight to all coalfields, by calculating average values for the coalfields separately and then averaging them. It is also interesting to note that the same value is obtained if, from the 79 samples, those with the highest contents of pyrites, carbonate minerals or carbonaceous matter in the extracted material (and therefore the less reliable) are excluded.

Table 4. Bias introduced into calculations of mineral matter and calorific values (d.m.m.f.) by use of various factors

'Shale' ash per cent	Calorific value (dry basis) B.t.u./lb.	Bias in mineral matter per cent					
		National average (1·13)	National average rounded to one place of decimals (1·1)	King, Maries and Crossley factors			
				England and N. Wales	South Wales		Scotland (1·13)
					Steam and bituminous (1·07)	Anthracite (1·07)	
5	—	0	− 0·15	− 0·20	− 0·30	− 0·30	0
10	—	0	− 0·30	− 0·40	− 0·60	− 0·60	0
		Bias in calorific value, B.t.u./lb					
5	14000	0	24	32	48		0
	14500	0	25			49	
10	14000	0	52	70	105		0
	14500	0	54			109	

The possibility that the factor could be rounded off to one place of decimals has been considered. *Table 4* shows the effect of this rounding off on the values for mineral matter and calorific value (dry, mineral matter-free basis) at two levels of 'shale' ash, i.e. 5 per cent and 10 per cent and national levels of calorific value 14000 of B.t.u./lb for steam and bituminous coals and 14 500 B.t.u./lb for anthracite. The effect of using the various KMC factors compared with the suggested value of 1·13 is also shown in the table. The method of calculation is given in the Appendix.

It will be seen that the factor involving only one place of decimals and those used by King, Maries and Crossley lead to biases which are not acceptable for the assessment of mineral matter content and hence calorific value on the dry, mineral matter-free basis.

It is therefore now recommended that for all British coals the one factor 1·13 should replace those previously in use in the KMC formula for the correction for loss of water of constitution of hydrated silicates.

Table 5. Limits of errors using the revised factor 1·13

'Shale' ash per cent	*95 per cent limits of error*	
	For calculation of original 'shale' (per cent)	*Contribution to calculation of calorific value (d.m.m.f.) for coals having a calorific value (dry) of 14 000 B.t.u./lb*
5	± 0·17	± 30
10	± 0·33	± 60

Table 5 gives estimates of the errors to be expected if this factor is used to calculate original 'shale' from 'shale' ash. The contribution of this calculation to the overall error of the estimate of calorific value (dry, mineral matter-free) cannot be determined precisely but approximate estimates have been derived and are shown in *Table 5*. The method of calculation is given in the Appendix. The substitution of the term 1·13 ash for 1·09 ash in the general KMC formula does not lead to any alteration in the factors for pyritic sulphur, sulphur in ash and sulphate in coal when these are expressed to one place of decimals. In considering the effect on the factor for carbon dioxide it is necessary to bear in mind the results of recent work on the carbonate minerals in coal. It is now thought that the use of a separate term 0·7 CO_2 for South Wales coals is unwarranted and that for all British coals the factor should be 0·8 CO_2. The revised formula, applicable to all coals, is therefore

$$\text{Mineral matter} = 1{\cdot}13\ \text{ash} + 0{\cdot}5\ S_{pyr} + 0{\cdot}8\ CO_2 - 2{\cdot}8\ S_{ash} + 2{\cdot}8\ S_{\text{sulphate in coal}} + 0{\cdot}5\ Cl$$

In the simpler modification of the KMC formula derived by Brown, Caldwell and Fereday[6] only a slight alteration to the coefficient for ash is necessary, this formula becoming

$$\text{Mineral matter} = 1{\cdot}10\ \text{ash} + 0{\cdot}53\ S_{total} + 0{\cdot}74\ CO_2 - 0{\cdot}32$$

XUM

This formula is also applicable to all coals.

Modifications to the corrections of volatile matter on the dry, mineral matter-free basis are necessary following the results of the present work. These are dealt with in a subsequent paper.

APPENDIX

Calculation of bias shown in Table 4

For each analysis of material extracted on milling shown in *Table 2* the 'error' involved in using the mean factor 1·13 to calculate original 'shale' from 'shale' ash instead of that actually determined is given by

$$\text{'Shale' ash} \times 1{\cdot}13 - \text{'shale' ash} \times \text{determined factor}$$

Because 1·13 is the mean value these 'errors' are, of course, random and summate to zero, over the whole set of observations. If any other factor F were used the 'error' would be

$$\text{'Shale' ash} \times F - \text{'shale' ash} \times \text{determined factor}$$

and the sum of such 'errors' would not be zero, i.e. the factor would introduce a bias into the final results. The size of this bias is given by the difference between these 'errors', i.e.

$$\text{'Shale' ash} \times 1{\cdot}13 - \text{'shale' ash} \times F$$

This expression is the same for all determinations. As the terms in the KMC formula are additive the bias in the calculation of original 'shale' is reflected in the final mineral matter value.

The estimation of the effect on calorific value (dry, mineral matter-free) of changes in this factor is not as straightforward, but since original 'shale' is usually the largest component of the mineral matter it can be shown that the bias involved is given approximately by the expression

$$\text{Calorific value (dry)} \left[\frac{100}{100 - \text{'shale' ash} \times 1{\cdot}13} - \frac{100}{100 - \text{'shale' ash} \times F} \right]$$

Examination of 'error' involved in calculation of original 'shale' from 'shale' ash

Within the limits of experimental error the amount of the original 'shale' is linearly related to the amount of 'shale' ash. The equation of the best straight line is

$$\text{Original 'shale'} = 1{\cdot}11\ (\text{'shale' ash}) + 0{\cdot}2$$

It can be shown, however, that the use of the expression

$$\text{Original 'shale'} = 1{\cdot}13\ (\text{'shale' ash})$$

does not increase materially the errors involved in the estimation of original 'shale'. The factor of 1·13 is thus the best overall estimate of the ratio of original 'shale' to 'shale' ash. The actual values of this ratio obtained for individual samples are shown in *Table 2*.

If the expression is used to calculate original 'shale' the estimates will have a standard deviation of 1·155 (with 78 degrees of freedom) and 95 per

cent confidence limits of $\pm$ 0·03 in the factor and $\pm$ 2·31 per cent in the value for original 'shale'. These limits for original 'shale' are, of course, still expressed as a percentage of the 'material extracted on milling'. They can be expressed approximately in terms of 'shale' ash by using the mean 'shale' ash value from *Table 2* (based on the values of '*b*' in this table), which is 69·8 per cent, thus

$$\pm 2{\cdot}31 \times \frac{100}{69{\cdot}8} = \pm 3{\cdot}31 \text{ per cent (of 'shale' ash)}$$

or, more conveniently, as $\pm$ 0·17 per cent of the original coal if the coal contains 5 per cent of 'shale' ash, or $\pm$ 0·33 per cent if the coal contains 10 per cent of 'shale' ash.

The calculation of similar limits for calorific value (dry, mineral matter-free) can again only be approximate but at the same two levels of 'shale' ash and with a calorific value (dry) of 14000 B.t.u./lb the contribution of the 'errors' in the original 'shale' calculation to the overall 'errors' in the estimate of calorific value are roughly $\pm$ 30 B.t.u./lb where the 'shale' ash value is 5 per cent and $\pm$ 60 B.t.u./lb where it is 10 per cent.

Mr K. Hand carried out most of the analytical work on which the paper is based. Acknowledgements are due to Mr H. Thomas for some of the earlier determinations, and to Mrs J. Jones and Mr H. W. Pearson for the collation of analytical data. The mathematical treatment was suggested by Mr I. Berkovitch and the computations of bias and estimations of error shown in Tables 4 and 5 and detailed in the Appendix were made by Mr H. J. G. Whitton. The paper is published by permission of the National Coal Board.

Coal Survey Laboratory,
Old Government House,
20 Dee Hills Park, Chester

(*Received May 1957*)

REFERENCES

[1] KING, J. G., MARIES, M. B. and CROSSLEY, H. E. 'Formulae for the calculation of coal analyses to a basis of coal substance free from mineral matter.' *J. Soc. chem. Ind., Lond.* 55 (1936) 277T

[2] NELSON, J. B. 'Assessment of the mineral species associated with coal.' *Mon. Bull. Brit. Coal Util. Res. Ass.* 17 (No. 2) (1953) 41

[3] FLINT, D. 'The total mineral matter in coal and its influence on coal classification.' *Mon. Bull. Brit. Coal Util. Res. Ass.* 17 (No. 4) (1953) 133

[4] RADMACHER, W. and MOHRHAUER, P. 'Die direkte Bestimmung des Mineralstoffgehaltes von Steinkohlen.' *BrennstChemie* 36 (15/16) (1955) 236

[5] GABSDIEL, W. 'Die Ermittlung der Mineralgehalter in Kohlen unter besonderer Berücksichtigung der anorganisch gebundener Wassers.' *Bergakadamie* 7 (1955) 481

[6] BROWN, R. L., CALDWELL, R. L. and FEREDAY, F. 'Mineral constituents of coal.' *Fuel, Lond.* 31 (1952) 261

[7] 'Analysis and testing of coal and coke.' *B.S. 1016*, British Standards Institution:, London 1942

[8] PARR, S. W. and WHEELER, W. F. *Bull. Eng. Exp. Sta. Univ. Ill.* 37 (1909) 1

[9] FIELDNER, A. C. and SELVIG, W. A. 'Present status of ash corrections in coal analysis.' *Trans. Amer. Inst. min. (metall.) Engrs* Coal Div. 88 (1930) 597

[10] 'Classification of coal by rank.' *A.S.T.M. Stand.* Part 3 (1939)

[11] MOTT, R. A. and WHEELER, R. V. 'The inherent ash of coal.' *Fuel, Lond.* 6 (1927) 416

XUM

Recent Developments and Notes

MECHANISM OF COKING

An account has been given by D. W. VAN KREVELEN of an investigation into the mechanism of the softening and degasification of coal, using the Gieseler plastometer, the Audibert–Arnu dilatometer and the thermobalance [*Brennst-Chemie* 37 (1956) 101; translation by Z. K. A. MOSZYNSKI, British Coke Research Association, Intelligence Section].

The problem was approached by seeking a system of substances of known composition which would show the same behaviour on heating, as indicated by plastometer and dilatometer curves, as bituminous coal. The criteria adopted for such a system were: (*i*) the mass must soften within a certain temperature range, (*ii*) the evolution of gas should take place within the same temperature range, (*iii*) the condensation reaction should be effected in the plastic state, so as to allow all the system to solidify. The fulfilment of the last condition was regarded as being very important, otherwise no residual dilatation and no re-solidification take place. A system fulfilling these requirements was found in a mixture of three components, (*a*) a linear polymer with satisfactory plasticity in a fixed range of temperature, novolak of phenolformaldehyde type, with a softening point of about 65°C; (*b*) a gas-liberating substance, 2,2-azo-di-*iso*butyronitrile, which liberates nitrogen at about 80°C, and decomposes in the same temperature range; (*c*) a complex branched substance, hexamethylenetetramine, which liberates ammonia. The ratio of these three components in the mixture was 5 : 1 : 1.

This system of substances was found to show, in the range 65 to 100°C, plastometer and dilatometer curves completely analogous to those of bituminous coal in the range 360 to 430°C, and the form and position of the curves as functions of the rate of heating show exactly the same regularity as in the case of coal.

It is concluded that all the observations point to the correctness of the 'thermo-bitumen' theory for the explanation of the plastic phenomena of coal. According to this theory, the plasticity is to be attributed to metastable products formed by the initial pyrolysis. This primary pyrolysis can be regarded as a depolymerization of a macromolecule, and this view is supported by the analogy between the products of pyrolysis and those of hydrogenolysis and extraction. All these products show a great similarity of structure to bituminous coal, although they have a relatively low molecular weight. The chemical reactions of the primary degasification are very closely linked with the plastic stage. Recombination of the radicals formed by the primary pyrolysis may be looked upon as a process of 'internetting' between multiple aromatic nuclei, and this results in re-solidification. This is immediately followed by further decomposition in which mostly methane and hydrogen are liberated and this secondary degasification leads to coke.

HYDROGENATION REACTIONS

A *Thesis* has been written by J. J. T. M. GEERARDS for the degree of Doctor of Technical Science of the Technical High School of Delft, describing the results of an investigation which was directed by Professors H. I. Waterman and D. W. van Krevelen. This research was concerned with the action, in the presence of iodine, of hydrogen on bituminous coal, carbohydrates and aromatic substances at temperatures between 300° and 400°C and in the absence of a liquid medium.

From a high-rank coal with a carbon content of 89 per cent, liquid hydrocarbons with a low oxygen content were prepared. The yields, 30 to 35 per cent by weight, were improved by a short period of pre-oxidation with air in a fluidized bed at 230°C. By the use of certain iodine compounds oxygen-free oils were obtained from the coal, whereas bromine compounds of similar type yielded only pitches of high molecular weight. The *n–d–M* method was used for the analysis of the oils which were found to be polycyclic, having between two and four rings per molecule. The molecular weights varied between 175 and 250.

The behaviour of some aromatic compounds under various decomposition conditions was compared with that of the bituminous coal extracts. The latter were found to behave in the same way with respect to iodine as phenanthrene and chrysene. It is suggested, therefore, that the coal extracts had probably a phenanthrene-like structure.

Carbohydrates such as sugar, cellulose and wood with about 50 per cent of oxygen by weight, treated with hydrogen in the presence of iodine, were found to yield oxygen-free oils which consisted of condensed-ring systems of 3 to 5 rings per molecule, the molecular weight varying from 250 to 400.

The influence of rank on the quantity and composition of the bituminous coal extracts was studied. The yield of extract decreased with increasing rank to almost nil with coals of 92 per cent carbon content. A diagram was developed with the aid of which it appears possible to determine the structure of saturated bituminous coal extracts, given the refractive index and density.

BROWN COAL GASIFICATION IN AUSTRALIA

The Gas and Fuel Corporation of Victoria came into being at the end of 1950, the chief reason for its formation being to provide finance to make possible the use of the brown-coal resources of Victoria for town gas production. Of the total probable reserves of about 61×10^9 tons of bituminous and brown coal in the whole of Australia, 44×10^9 tons are brown coal, situated in Victoria. The brown-coalfield in the Latrobe Valley is the largest and most readily accessible deposit in the world. The coal is won by open-cut mining operations, it is very earthy in nature, with high moisture and oxygen contents, very friable and highly reactive, which cause it easily to ignite spontaneously, and it is non-caking. It can be regarded as a material which, by drying and briquetting, can be upgraded into a fuel that can compete with black coal in nearly all spheres of usage. On the development of these reserves of brown coal depends Victoria's industrial future and there has recently been described by R. S. ANDREWS, Chairman and Managing

XUM

Director of the Gas and Fuel Corporation of Victoria, a major project in gas manufacture in order to utilize these immense reserves of brown coal in the State [*Publ. Instn Gas Engrs, Lond. No. 503* (1957)]. The scheme that is outlined represents the first attempt in the British Commonwealth to depart from conventional methods of town gas production.

The various possible methods of gasification were considered and a decision was taken in favour of the Lurgi high-pressure process. A plant was erected at Morwell, 93 miles from Melbourne, and came into operation towards the end of 1956. The initial output of the plant will be about 15 to 18×10^6 ft^3 of gas per day, and it is planned to bring production to 30×10^6 by 1960 and 60×10^6 by 1965. The anticipated performance target is: gas composition—CO_2 2·0, O_2 0·2, C_nH_m 0·3, CO 21·8, CH_4 19·1, C_2H_6 0·4, H_2 53·9, N_2 2·3 per cent; calorific value—446 B.Th.U./ft^3; gasification efficiency—81 per cent; gas yield per ton of briquettes—34 000 ft^3.

Whilst the conditions in Victoria are favourable for the introduction of complete gasification, the process which has been embarked upon there opens up new possibilities which prevent the gas industry generally from being confined to the use of the diminishing reserves of caking coals.

HARD COKE FROM BROWN COAL

The Gas and Fuel Corporation of Victoria, Australia, is at present erecting a semi-commercial plant at Morwell, for the purpose of producing a 'hard char' from brown coal (see previous note) which is to be tested on a large scale for its value in metallurgical industries.

This project has arisen as a development of investigations in the University of Melbourne in the last few years, under the direction of Professors P. L. Henderson, H. K. Worner and Hill Worner. In the usual Lurgi *Spühlgas* process the extrusion brown-coal briquettes yield a 'hard char', but this is not entirely satisfactory for metallurigcal processes. It was found in these investigations that with controlled rates of heating in two stages of carbonization a 'hard char' could be produced from the briquettes, having a mechanical strength equal to that of the best metallurgical coke. During the drying period, up to 200°C, the temperature was raised 40°C per hour, from 200° to 600°C, 100°C per hour, and from 600° to 800°C, as rapidly as possible. This 'hard char' has low ash and sulphur contents, its bulk density is 20 per cent higher than that of normal metallurgical coke and it is highly reactive. It is thought that this new fuel might have revolutionary influence in a variety of metallurgical processes.

REACTIVITY AND POROUS STRUCTURE OF COKE

M. Bastick, M. Moutach and H. Guérin have written a further paper on the results of their investigations into the connection between the reactivity of coke and the development of internal surface under the action of carbon dioxide or steam [*C.R. Acad. Sci., Paris* 243 (1956) 1764].

In a previous paper [*C.R. Acad. Sci., Paris* 240 (1955) 2524] they had shown that gasification produces true activation and that the reactivity depends on the surface area but is not proportional to it. In other words, the speed of gasification per unit area is not constant.

In the later work these investigators have studied how the internal surface of a coke was distributed between different-sized pores at various stages of gasification with carbon dioxide or steam. Their results show that as the coke is progressively consumed, the total surface first increases rapidly, reaching a maximum value when about 24 per cent of the coke has been consumed, and then decreases. The average pore size steadily increases throughout the reaction. This growth of surface is due to the creation of small pores, of diameter less than 50 Å, which arise either from the opening up of pre-existent pores which were obstructed by fine particles produced by breakage, or from the preferential combustion of active centres.

Carbon dioxide appears to react less in the small pores into which it does not penetrate so far and this difference can be attributed to the fact that carbon dioxide has a higher overall rate of reaction than steam and consequently there is not time for penetration far into the small pores. Activation by steam is more effective than by carbon dioxide for the more reactive cokes in which numerous long slender pores can be developed. This difference diminishes with the reactivity when the variations of this amongst different cokes are chiefly due to the development of internal surfaces for which the small pores are mainly responsible. It is concluded that the reactivity of a coke depends essentially on its ability to produce small pores when it reacts with carbon dioxide or steam.

WASTE GAS PLUMES

Two papers were presented recently to the Institute of Fuel dealing with the rise of waste gas plumes from industrial chimneys [*J. Inst. Fuel* 30 (1957) 322, 329; Discussion, 333].

The first of these papers, by C. H. BOSANQUET, Imperial Chemical Industries Ltd, Billingham Division, presents a method for calculating the rise of a waste gas plume due both to its velocity of emission and its thermal buoyancy. It is assumed that when a cloud of hot gas is rising the total heat content and total momentum are not affected by dilution with atmospheric air. It is also assumed that the upward momentum increases at a rate proportional to the surface area of the cloud multiplied by a function of the wind velocity and the velocity of the cloud relative to the surrounding atmosphere. An equation is developed for finding the track of hot waste gas rising from a chimney in a wind of any velocity. The height to which the waste gas rises depends on both its heat content and its exit momentum. It is shown that if the temperature gradient in the atmosphere is less than adiabatic the smoke will not continue to rise indefinitely but will eventually settle down at a definite height.

The second paper, by A. C. BEST, Meteorological Office, London, deals with the ground level concentration of gas emitted from a chimney which reaches a maximum value at a particular distance downwind from the chimney. Distance and concentration depend on the design characteristics of the chimney and on the meteorological conditions. If the height to which the plume of gas rises is known, the maximum concentration in any weather conditions can be calculated. It is this maximum concentration which is of interest when the stack is being designed.

XUM

Three of the formulae which have been proposed for computing the height of rise of plume are considered, one due to O. G. SUTTON, the Oak Ridge formula, and another due to C. H. BOSANQUET. The formulae of Sutton and of Bosanquet are based respectively on experimental field work and on laboratory work. The Oak Ridge formula is purely empirical and expresses the results of a number of full scale observations. For the purpose of computing maximum ground-level concentration the three formulae are in reasonable agreement, and the Oak Ridge formula has the merit of being simple and sufficiently accurate.

INDUSTRIAL GAS DEVELOPMENTS

The Industrial Gas Development Committee has recently issued a series of reports of new devices in connection with the use of gas for different purposes. Amongst these are a unit comprising a system of automatic ignition and flame failure protection, and an immersion tube heated tank for bulk hot water supply, both of these having been developed by the North Western Gas Board. The West Midlands Gas Board has been responsible for a large scale conversion from producer gas at a works in which there were sixteen reverberatory aluminium holding furnaces which were re-designed to operate on town gas. A zero outlet governor, a multi-tray oven for low temperature heating of solids, a pipe bending forge, a plant for drying separate plates for dry accumulators, and a hot food cabinet, are described in reports from the North Thames Gas Board. A gas fired steam superheater has been developed by the South Eastern, and an aluminium fluoride drying plant by the South Western Gas Board.

COAL SCIENCE

The second International Conference on Coal Science under the presidency of D. W. VAN KREVELEN, was held in Limburg, the Netherlands, during 1 to 4 May 1957. The proceedings, including the discussions, are to be published in *BrennstChemie*, and a summarized account of the conference has already been published [*Nature, Lond.* 180 (1957) 417]. All the papers presented to the conference were concerned with experimental advances and a notable feature was the increased proportion of work based on new approaches and departing from traditional lines of coal research (see p. 111).

PREMIUM GRADE GASOLINES FOR THE FUTURE

The compressión ratios of petrol engines average 9 to 1 at present, with about 6 per cent of motor car engines in use having ratios around or above 10 to 1. This percentage is expected to increase rapidly and the average ratio to be 11 to 1 by 1961. In order to meet the full requirements for such engines, probably involving an average octane number of 105 (F–1 research method) by that date, it is predicted that isomerization processes will be widely used to make the high octane motor fuel components.

High octane fuels have been made in the past few years mostly by catalytic cracking, catalytic reforming and alkylation. But in the past year or so considerable attention has been given to developing or improving several direct isomerization processes for this purpose. The catalyst is usually a noble metal or aluminium chloride. Reaction temperature varies within the

range 95° to 480°C, pressures from 10 to 55 atm, residence time from 10 to 40 minutes. Typical feed stocks include straight-run naphthas or natural gasoline [*Industr. Engng Chem.* (*Industr.*) (No. 8, 1957) 23A].

COAL MINES LEGISLATION

The *Coal Mines Act 1911* remained in force for over forty four years with minor amendments. Some safety provisions, however, were kept up to date by regulations made under the *Act*. With developments in mining science and the increasing use of machines for winning coal it became apparent just before the 1939–45 war that a new safety code for mines was required. A Royal Commission on Safety in Coal Mines was appointed under the chairmanship of Lord ROCKLEY to study the general subject of safety in mines. It issued its report in December 1938, But the work begun, as a result of its recommendations, on the preparation of a new code was suspended on the outbreak of war and not resumed until 1951.

Within this period, on 1 January 1947 the coal industry became nationalized and thereby there arose the problem of drawing up provisions of an *Act* to be operated by a huge organization with a large and complex system of management. At the same time the nationalization of the industry gave the opportunity for the planning and undertaking of safety measures and the re-equipping of the whole industry from a national viewpoint. Accordingly the new *Act*, the *Mines and Quarries Act 1954*, both consolidates and amends much of the old law and also introduces a number of new provisions, in particular the measures concerning ventilation and dust precautions.

An edition of the *Act* with a summary of its provisions and considerable annotations has just been published. The author of this work is J. R. PICKERING, of the Inner Temple and North-Eastern Circuit, Barrister-at-law [Butterworths: London, 1957].

BRITISH STANDARD FOR OIL FUELS

Since 1937, when *B.S. 742* was first issued, there have been separate British Standards for fuels for oil engines (*B.S. 209*) and fuel oils for burners (*B.S. 742*). It has been considered, however, that the perpetuation of two standards is unnecessary in view of the increasing use of burner fuels in oil engines. One standard has therefore now been published, *B.S. 2869: 1957, Oil Fuels*, in which the specifications of all the oil fuel grades and test methods are collected together. The specification section of the standard consists of three parts, dealing with engine fuels, domestic fuels, and industrial and marine fuels.

A considerable number of modifications have been made to the previous standards in order to bring them into line with current practice. A significant modification is the reduction of the minimum flash point temperature from 150° to 130°F for oil fuels Classes A and D. Consideration has been given to the specification of Ramsbottom carbon instead of Conradson, but in view of the inadequate correlation between these two tests at the present time, the substitution of Ramsbottom values has been deferred until a later date.

XUM

OIL FROM COAL IN AUSTRALIA

It is announced that an oil-from-coal plant comparable to the 'SASOL' plant in South Africa is to be set up in Australia. The plant is expected to be in operation within five years and is to produce oil and high-octane petrol from brown coal at Morwell, Victoria. The initial target is to be 30000 tons per annum of oil and petrol, sufficient to meet the needs of all farm equipment in Victoria. It is stated that the synthetic liquid fuels will be produced at a cost which will compete economically with natural products.

HEAT GENERATION IN COAL

P. C. NEWMAN, of the National Coal Board, Stoke Orchard, has proposed a new method for measuring the generation of heat in coal or other finely divided powders [*Brit. J. appl. Phys.* 8 (1957) 162]. The information obtained from such measurements is desirable in connection with work on the constitution of coal and is also required for the design of oxidation plant and for the consideration of the safety of stored coal.

A method of measuring heat generation was developed in which no attempt was made to work under adiabatic conditions, but in which heat fluxes in the system, which could be correlated with heat generations, were deduced from measurements of temperature difference in the coal itself. This is practicable since powdered coal has such a low thermal conductivity that very small heat fluxes can give rise to readily observable temperature differences.

The paper describes an apparatus in which the rate of heat generation was measured in powdered coal exposed to gases containing a varying proportion of oxygen at temperatures in the range 15° to 150°C. A reasonable external specific surface was provided by the use of powdered coal, but even so it was necessary to detect rates of heating as small as 0·03 cal/g of coal/h, i.e. about $6{\cdot}7 \times 10^{-6}$ cal $cm^{-3}s^{-1}$. The thermal conductivity involved was of the order 10^{-3} to 10^{-4} cal cm^{-1} $sec^{-1}°C^{-1}$ and the diffusivity 10^{-2} to 10^{-3} cm^2/s.

New solutions to the heat flow equation for heat generation in cylindrical and spherical bodies as required for calculating the result are given in the paper and the suitability of the method was experimentally confirmed.

SHALE OIL

In May 1957 the Union Oil Co. of California started up a very large prototype oil shale retort near Grand Valley, Colorado [*Chem. Engng* 64 (No. 9) (1957) 146]. Its capacity is 300 tons of shale per day and the cost 1·5 million dollars. The objective is to establish whether oil shale can be mined and retorted and the oil refined at a cost which is competitive with the production of refined petroleum products.

The oil shale at Grand Valley is of high quality and yields about 30 gal of oil per ton. In the retort used here the crushed shale enters at the bottom from a hopper that feeds an oscillating-reciprocating 'rock pump'. The pump action effects the entire upward movement of the shale. The maximum conservation of heat is provided for in the operation of the retort and no cooling water is needed as all heat transfer related to retorting occurs within

the unit. The entering air is preheated by the hot ash before reaching the combustion zone where it burns the carbon residue in the spent shale.

Flue gas from the combustion zone at 1200°C gives up its heat to preheated shale fragments, cracking the kerogen to gases and oil vapour at about 430°C. The hot vapour–gas stream, moving countercurrent to the shale, cools until the oil vapour condenses on the incoming shale. By the time the gas and oil streams are discharged from the retort they are only slightly above ambient temperature.

COKE BURNING APPLIANCES

In 1938 the London and Counties Coke Association published a handbook of approved coke-burning appliances for domestic use. Since then further editions have been issued and recently the Gas Council has published the fifth edition [*Coke Burning Appliances*, The Gas Council, Coke Department: London, 1957, 410 pp]. The new handbook has been compiled under the direction of the Coke Technical Committee and a particular object in producing this edition has been to give assistance to those concerned with the application of the *Clean Air Act*. Full technical information is given on about 300 tested and approved appliances, and for the first time in such a handbook data are given on the rated output or room heating capacity of each appliance.

TEST FOR COKE STRENGTH AT HIGH TEMPERATURE

M. O. HOLOWATY and C. M. SQUARCY presented a paper to the AIME Blast Furnace, Coke Oven, and Raw Materials Conference at Pittsburgh, in April 1957 on the development of a high temperature compression test for blast furnace coke [*J. Metals, N.Y.* 9 (1957) 577]. This test to predict coke performance in the blast furnace was designed to overcome the lack of correlation between performance and the results of conventional tumbler stability and hardness tests carried out at room temperature.

The apparatus consists essentially of a graphite crucible to accommodate the test specimen of coke in the form of a $\frac{1}{4}$ in. cube. A thick graphite cover on the crucible is provided with three holes to accommodate the 2 in. diameter pressure rod, determination of the temperature by an optical pyrometer, and a porcelain tube to deliver nitrogen to the system. The crucible is suitably fixed in a refractory block provided with heating coils. The compression rod is lowered on to the specimen on the bottom of the crucible and immediately counterbalanced on a lever system with lead shot, so that no pressure is applied to the sample prior to the actual compression test at 1650°C. About 20 minutes is required to raise the temperature to this value which is maintained while the pressure is increased by pouring lead shot into the lever arm container. A sudden plunge of the lever arm indicates the collapse of the coke specimen.

Experiments conducted in this apparatus show that there is a high degree of correlation between high temperature strength properties and blast furnace output. The test can be regarded as simulating conditions encountered by the burden in the high temperature zone of the blast furnace.

XUM

NEW REFINING PROCESSES FOR BENZOLES AND NAPHTHAS

Investigations, which have been carried out by the Coal Tar Research Association during the past few years on the refining of crude benzole and naphthas, have led recently to the erection of a pilot plant by Newton Chambers and Co. Ltd, of Thorncliffe, near Sheffield, for the commercial development of a new process devised by the C.T.R.A.

At the present time the refining of benzoles and naphthas depends on the use of strong sulphuric acid in an intermittent batch process and entails considerable loss of spirit. In the new process there is an increased yield of motor spirit with a normal loss of only 1 to 2 per cent as compared with 15 to 20 per cent loss with sulphuric acid washing. There is also greater purity of the product and there is no 'acid tar', the disposal of which is very difficult.

The new process is a hydro-refining one developed for continuous operation which can be completely automatic to ensure that the refined products are consistently in accordance with the designed specification. Pure hydrogen or hydrogen-containing gases such as coke-oven gas are used in combination with a catalyst for the preferential hydrogenolysis of sulphur compounds and gum-forming olefines. The process gives a substantially theoretical yield of refined products. It differs from other hydro-refining processes for crude benzole by using a considerably shorter contact time, consequently giving a higher output for a given size of converter, and in operating at considerably lower pressures for naphtha refining. The reduced amount of hydrogen required for naphtha refining results in minimizing the undesirable conversion of aromatics to naphthenic hydrocarbons.

A new plant for the catalytic refining of benzole was put into operation in November 1956 at Installation des Houillères du Bassin de Lorraine à l'Usine Centrale à Benzol de Carling. The catalyst is a molybdenum compound on alumina, and the crude benzole vapour, mixed with three times its volume of coke-oven gas, is passed over the catalyst at 300° to 360°C and at a pressure of 110 to 154 lb/in². This hydro-refining plant is said to be unique in its use of coke-oven gas, as other plants use hydrogen obtained from coke-oven gas by liquefaction and fractionation [A. THOMAS. *J. Usin. Gaz* 81 (1957) 203].

PETROGRAPHY OF AMERICAN COALS

The work of the late Reinhardt Thiessen (1867–1938), pioneer American coal scientist, in promoting fundamental studies of coal was outstanding both in its magnitude and results. During his association with the U.S. Bureau of Mines from 1910 until his death he was engaged in microscopical and chemical investigations of lignite and bituminous coals. To solve the problem of obtaining translucent sections of bituminous coals, he used techniques employed in petrography laboratories for grinding specimens of rock to microscopic thinness. Although this technique, as applied to coal, was not new, it had not previously been tried with American coals. As a result of his work in this field Thiessen developed his well known system of terminology for the microscopical description of coal, and his papers on the origin and constitution of coal, which brought him world-wide recognition as an authority, were illustrated with remarkably fine photomicrographs. Later, with his assistants,

he devised a method of systematically assaying a coal bed by obtaining thin sections of a complete column sample and petrographically analysing the sections both qualitatively and quantitatively. It thus became possible to integrate coal petrography with other investigations which were being made by the Bureau of Mines on the coke and gas-making properties of American coals. The reports of this work, published between 1931 and 1943, include the results of systematic petrographic studies of 34 bituminous coals of the Eastern and Interior coal fields. Thiessen can be regarded as the first to establish work in coal petrography on a sound and practical basis.

Since the beginning of these petrographic investigations in 1930, leading to the microscopical evaluation and classification of coals, more than 217 coals of varied rank, type and source have been studied. The knowledge which has been gained of the petrographic composition of these coals, when associated with other laboratory information, is helping considerably in improving methods for the preparation and utilization of the coals. It has seemed desirable, therefore to assemble in a single publication all the Bureau's information on this subject. This has recently been done in the publication 'Petrography of American Coals', by B. C. PARKS and H. J. O'DONNELL [*Bull. U.S. Bur. Min. No. 550* (1956)].

CARBON RESIDUE IN OILS

A panel of the Institute of Petroleum has recently issued a report on its deliberations during the past three years on the determinations of carbon residue in oils by the Ramsbottom and Conradson methods [*J. Inst. Petrol.* 43 (1957) 292]. It is concluded that there is a correlation between Conradson (C) and Ramsbottom (R) results on whole fuels and 10 per cent bottoms which can be represented by

$$R = 0{\cdot}133 + 0{\cdot}8397\,C$$

where the R and C values of carbon residues are in per cent by weight. There appears to be little difference between the confidence which can be placed on determined and calculated Ramsbottom results, but more confidence can be placed on determined Conradson values than on those calculated. This is believed to be due to a systematic error in the Ramsbottom method of test greater than any such error in the Conradson. The panel recommends that the correlation between results of these two methods should not be adopted at present; that the Conradson test should not be deleted from *Standard Methods;* that the existence or otherwise of a systematic error in results obtained by the Ramsbottom method should be confirmed and if such error is found, a more rigorous specification should be made for the procedure and/or the apparatus.

NEW FUEL RESEARCH STATION

The Fuel Research Station at Greenwich is being replaced by a new station which is now being built at Stevenage in Hertfordshire. It is hoped to start occupation in the autumn of this year and to complete the station in the spring of 1959. There will be a non-industrial staff of about 220 and an industrial staff of about 120. The estimated cost is about £750 000.

XUM

In the light of a review made by the Research Council of the Department of Scientific and Industrial Research, of the present-day needs for fuel research, the programme of the new station will differ markedly from that of the old. Many of the programmes of research carried out in the past at Greenwich are now being undertaken by the nationalized industries, and by government and industrial research organizations. As a result the activities to be transferred to the station at Stevenage will be limited to reactions between carbon monoxide and hydrogen to produce synthetic oils and chemicals, and work on atmospheric pollution and its prevention. The work of the new station will not be confined to fuel research, but it will include a number of other subjects such as research into mineral processing, in view of the need to examine new methods for the treatment of low-grade complex ores. The head of the new station will have the title of Director of Fuel and Process Research.

THE DALTON LECTURE

The tenth Dalton Lecture, sponsored by the Royal Institute of Chemistry, was given in Manchester on 25 October by J. BRONOWSKI, Director of the Coal Research Establishment, National Coal Board, Stoke Orchard, Cheltenham. His subject was *Coal and Coal Chemicals in the National Economy*. The lecturer said that if industry was to use coal for what it was, the most important chemical raw material in Britain, then the decisive moment had come. It is necessary now to plan a long-term conversion of much of our coal from a crude source of energy to special fuels and chemicals. The change to atomic power will set free for the production of chemicals the small and gassy coal now being mined. It is necessary to abandon the old conception that coal must be used as nearly as possible in the state in which it was mined. In the immediate future, much attention is being given to the utilization of non-caking high volatile small coal for the production of smokeless fuels. Atmospheric pollution is thereby prevented and valuable oils and chemicals recovered from the coal, as well as town gas for industrial and domestic use.

The new treatment of coal will centre on the use of a fluid bed of powdered coal through which hot gas is passed. At first this process would be used to make a char as a basis of briquetted smokeless fuel for domestic burning. Then the char might be gasified either for industrial use or for the synthesis of oils and chemicals. Another desirable mode of treatment of coal is with hydrogen, and the availability of cheap hydrogen for this purpose will be essential.

There are indications of serious gaps in the near future between supply and demand for chemicals such as benzene, toluene and naphthalene. These gaps may well be filled by using coal as the starting material.

COAL SEAM RESEARCH

A residential conference organized by the Institute of Fuel is to be held in the University of Sheffield from 15 to 17 April this year on the subject of *Science in the Use of Coal*. The communications at the sessions will deal with the physics and chemistry of coal, coal preparation and breakage, coal carbonization, combustion and gasification, reactivity of cokes and chars. Each session

will be introduced by a survey of the current position prepared by an invited author.

The first of the opening surveys, that by A. M. WANDLESS, Deputy Director of Scientific Control (Coal Survey), National Coal Board, has already been published [*J. Inst. Fuel* 30 (1957) 541]. This is a review of the properties of British coal seams, with suggestions for research. As regards future trends the basic overall characteristics of the seams worked are not likely to alter in the next eight years, that is, during the period of the short-term plan. Ash content will tend to rise slightly, also sulphur content. There is likely to be a slightly smaller production of prime coking coals, Rank Code 301, than at present. The most drastic change in this period is likely to be in coal size and and a very substantial increase in the tonnage of coal less than $\frac{1}{2}$ in. in size must be envisaged.

The author concludes with some suggestions for research. Knowledge of the hardness of coal seams, of their cleats and slips, of the bearing capacity of floor and strength of roof, is required so that machines used at the face may give high productivity and not break the coal excessively. Since run-of-mine coal is becoming dirtier, there is a field for inquiry to determine to what extent low-rank small coal should be cleaned for electricity generation. To provide solid smokeless fuel to implement the requirements of the *Clean Air Act*, it will be necessary to discover how to process satisfactorily cleaned low-rank small coal to give a number of smokeless end-products. Considerable progress in this direction has already been made at the Coal Research Establishment of the National Coal Board. Since there will be greater reliance on lower-rank coking–gas coals (Rank Codes 500 and 600) in blast-furnace coke-making there is an important field for research to discover more about the coking process so as to be in a position to make better use of these coals for coke production. With regard to sulphur in coal, if there were available an economic method of removing the finely dispersed iron pyrites in many seams which, but for their high sulphur content, would be of acceptable coking quality, our resources of coking coal would be in effect considerably increased.

NITRIC OXIDE IN COKE OVEN GAS

B. LEFRANÇOIS has studied the origin of nitric oxide in coke-oven gas and how to improve its elimination [*Chim. et Industr.* 78 (1957) 193]. He has shown that nitric oxide is formed from the nitrogen in the coal and atmospheric oxygen. The greater part of the nitric oxide arises from the air admitted to the oven with the coal.

The effect on the concentration of nitric oxide of adding very small amounts of *cyclo*pentadiene to coke-oven gas was studied. The concentration of nitric oxide was found to diminish after an induction period which became shorter as the amount of *cyclo*pentadiene increased. The same general effect was found when oxygen was added, but it did not occur with coke-oven gas containing no diolefines. The results of the investigations have led to an explanation of the way in which the amount of nitric oxide varies with time during carbonization of a charge of coal.

The study of the reaction has made it possible to improve the elimination

XUM

of nitric oxide from coke-oven gas. The so-called 'capacity' process which is used for elimination consists of the gas, under a pressure of 10 to 15 kg/cm², passing for 1 to 1·5 minutes through a chamber kept at 80° to 90°C. By adding a small quantity of air, corresponding to a content of 0·2 per cent of oxygen, to the gas before it enters the chamber, the elimination of nitric oxide is improved.

BONE–WHEELER MEDAL

The Council of the Institute of Fuel in 1956 decided to establish a new award to be known as the Bone–Wheeler Medal and Prize of the Institute, for the best paper on a subject within the purview of Fuel Technology, including the application of modern scientific techniques, by an author not over 33 years old on 1 September in the year of entry. The winning paper must be of a standard meriting publication in the *Journal*. By the generosity of the Board of the National Industrial Fuel Efficiency Service, a prize of £50 will accompany the Medal.

The first award of the medal has been made to A. M. FREEDMAN, who has worked for the past few years on problems associated with boiler availability and air pollution. He is at present engaged on work in the Boiler Department of the British Coal Utilisation Research Association.

COAL RESEARCH IN AUSTRALIA

The first issue of *Coal Research in C.S.I.R.O.* made its appearance in May 1957 and is devoted to current work in the carbonization field. This periodical is intended to give a picture of the fuel research work that is in progress in the Coal Research Section of the C.S.I.R.O., with emphasis on the practical applications of the work. A secondary objective is to stimulate interest in fuel technology and thereby help to increase the supply of fuel technologists to Australia. The laboratories of the Section are at North Ryde, near Sydney. The Section was established in 1948 to undertake, on a national basis, a long term fundamental and comprehensive study of the physical and chemical characteristics of Australian coals. A fairly detailed account of current investigations was given by H. R. BROWN, the Officer-in-Charge, to the Institute of Fuel, in October 1956 [*J. Inst. Fuel* 30 (1957) 137].

Investigations are being undertaken for the systematic measuring of parameters additional to those already well established for the characterization and evaluation of coals in the northern hemisphere. Hence detailed studies are being made of the petrographic constitution of coal seams, of the physicomechanical properties and combustion characteristics of coals, of the plastic behaviour of coal types and macerals, and of the nature and distribution of the mineral matter in coal.

Amongst recent reports issued by the Coal Research Section, in addition to several which deal with the washability and carbonization characteristics of coals from individual seams, there may be noted particularly reports on the determination of the inorganic constituents in Australian coals by rapid semi-micro (photometric) methods, the effect of pitch on the fluidity of coal, the calibration of the Gieseler plastometer in terms of absolute units of viscosity, the burning of some typical New South Wales coals in travelling-grate

stokers, and the influence of some physical factors on the structure and permeability of fuel beds.

In connection with the studies on devolatilization and degasification of coal, an outstanding contribution to the experimental techniques is the invention and development of a new type of differential thermogravimetric balance that has been developed by P. L. WATERS, of the staff of the Coal Research Section [*Nature, Lond.* 178 (1956) 324; *C.S.I.R.O. Coal Res. Sect. tech. Commun. No. 18* (September 1956)]. It is an automatic recording instrument that will detect and register weight variations of the order of a milligramme per minute. The instrument has been used in conjunction with the Gieseler plastometer and petrological studies to investigate the thickness of the plastic layer and the stages in the transition from coal to coke.

THE PROCESS OF CARBONIZATION

R. DIAMOND and P. B. HIRSCH, of the Cavendish Laboratory, Cambridge, in a paper to the conference on *Industrial Carbon and Graphite* (see above) described an investigation of the X-ray scattering from carbonized coals in a study of the low-temperature carbonization process, that is, up to 1000°C. The X-ray patterns have been interpreted in terms of the model of turbostratically packed small aromatic molecules assumed by H. E. BLAYDEN, J. GIBSON and H. L. RILEY in earlier work [*Proc. Conf. on Ultra-fine Structure of Coals and Cokes.* B.C.U.R.A.: London, 1944, p L76].

As a result of their work these investigators present this picture of the carbonization process. Up to about 500°C, a relatively high proportion of 'amorphous' material is lost, probably including OH and CH_2 groups. The removal of this material allows the crystallite layers to pack better. Between 500° and 600° growth of the layers sets in and this takes place by coalescence of neighbouring layers and a wide distribution of molecular sizes results. Probably due to this, the packing of the layers deteriorates. The rate of growth is approximately linear up to 1000°C. Cross linking of neighbouring layers takes place which accounts for the low hydrogen content of the carbons. The rate of growth of the layers is greater for the anthracites than for lower rank coals, probably because the layers are already in reasonably good alignment owing to their preferred orientation parallel to the bedding plane. Above 700°C the packing of layers improves again by gradual re-alignment. The growth of the layers is accompanied by the appearance of a large-scale porosity.

W. A. KIRKBY

COMBUSTION AND FLAME

Attention is drawn to the following *Notes* which readers of *Fuel* may find of interest in the December 1957 issue of *Combustion and Flame*:

Russian experiments on open-hearth combustion
Dust explosions
Fire research
New type boiler for oil refinery
Industrial jet-burner
Flames and industry

XUM

Obituary
Professor Walter Fuchs of Aachen

THE sudden death of Professor Walter Fuchs, Director of the Chemisch-Technisches Institut, Technische Hochschule, Aachen, on 30 August 1957, was a shock to all coal scientists.

Walter Fuchs was born in Vienna in 1891 and obtained his doctor's degree at the University of Vienna in 1914. From 1919 to 1926 he was *Privat Dozent* at Brünn University and between 1927 and 1931 Departmental Head at the Kaiser Wilhelm Institut at Mülheim/Ruhr, under the famous Franz Fischer. He then accepted in 1931 a professorship at the Institute of Technology in the University of Aachen. With the advent of Hitler he emigrated to the United States of America. In 1934 and 1935 he lectured at Rutgers University and from 1935 to 1942 at the Pennsylvania State College. Between 1942 and 1949 he acted as an industrial consultant in New York and then returned to Europe to resume his professorship at Aachen.

Throughout these years Professor Fuchs pursued an extremely active scientific career, having written six books and about 200 other publications. He started this career with research on lignin chemistry, which work, after a great many papers, resulted in the publication of his book *Die Chemie des Lignins* (Berlin, 1926). As a result of his work on lignin Professor Fuchs became interested in phenols and in coal chemistry; this resulted in a further book *Die Chemie der Kohle* (Berlin, 1931), which gave a great stimulus to coal research. Coal chemistry and lignin chemistry have remained two of his favourite objects of scientific work.

Professor Fuchs was endowed with a flexible mind, as is evident from his publications since 1945 in which he and his pupils deal with a great number of subjects in chemical engineering, with particular emphasis on applications of thermodynamics and reaction kinetics.

An important stimulus to coal science and coal technology was given by the organization, at the instigation of Professor Fuchs, of the annual *Steinkohlentagung* the first of which was held at Aachen in 1949. At these conferences many aspects of coal, including technological, chemical and even economical, were discussed. These *Steinkohlentagungen* were the basis for the 'International Conference on Coal Science', which was held in the Netherlands in 1955 and 1957 and was organized by an international committee of which Professor Fuchs was a member.

Thus, Professor Walter Fuchs has contributed largely to forming a wide circle of coal scientists who, in addition to his many friends and followers, will bear him gratefully in mind as a great scientist and an outstanding personality.

D. W. VAN KREVELEN

OVERSEAS CORRESPONDENTS' NOTES

The Editor is grateful for the following information on matters of present interest relating to meetings and other activities in the fuel science field which has been received principally from the respective overseas correspondents of the countries set out below.

CANADA

General

THE overshadowing activities in Canada relating to fuels during 1957, reports Dr D. S. MONTGOMERY, have been the planning and construction of long distance natural gas pipelines and the expansion of markets. Early this year Westcoast Transmission Company Ltd had completed 70 per cent of its 30 inch 650 mile line from Taylor, ten miles from Fort St John, to Vancouver and the United States border near Huntingdon. Trans Canada Pipe Lines Ltd had completed 10 per cent of the 34 inch line from Alberta to Ontario, with pipe deliveries almost complete. In addition, a 20 inch line from Toronto to Montreal was started and will supply gas imported from the U.S.A. to Montreal until the Trans Canada line is complete in 1958.

These two major pipeline companies will supply gas to give additional transmission and distribution systems. Obviously, in order to justify this tremendous construction, there has been much activity in expanding domestic and export markets. The rapid expansion of domestic markets now seems assured but there have been delays and obstacles to exporting to the U.S.A. Nevertheless, the expected heavy demand has spurred natural gas explorations.

With the increased use of this fuel, gas-gathering and processing facilities are expanding with a resulting increase in production of natural gasoline, butane, propane and sulphur. The prospects of larger supplies of by-product liquefied petroleum gases in the near future led to appraisals of the economic feasibility of building a products pipeline from Alberta to Winnipeg and Fort William.

The petroleum industry has maintained a rapid rate of growth. Last year the domestic market expanded by 13 per cent and exports expanded threefold to make Canada the eighth largest oil producer in the world with three per cent of world production.

The Athabasca oil sands have received periodic publicity but commercial development of this source of oil has not yet materialized. In the meantime, a new method of extracting bitumen by use of an inexpensive 'hydrogen donor-diluent' has been patented in the U.S.A. by the Esso Research and Engineering Co. The donor-diluent can be a low-cost material such as a partially hydrogenated thermal tar obtained from catalytic cracking operations. Transferable hydrogen from the donor-diluent upgrades the oil extracted from the sand.

The unparalleled activity in the natural gas and petroleum industries has been an important contribution to our national economy and has made Canada more self-sufficient for fuel.

XUM

In the face of strong competition, our coal industry has used every practical means at its disposal to maintain an established percentage share of the industrial fuel market but with limited success. High production and transportation costs and dieselization of railways have held industrial coal consumption to a fairly constant level during a period of industrial expansion. The result has been that coal dropped from 74·9 to 54·9 per cent of all industrial fuels consumed.

Furthermore, a high level of prosperity and high purchasing power has resulted in widespread use of natural gas and oil for domestic dwelling heating.

Mechanization of coal mining operations continues and production for all Nova Scotia collieries reached an all time high of 2·41 tons per man shift in 1956 as compared with 2·33 tons in 1955. Machines which have contributed to this improvement are the 'Dosco Miner', a continuous mining machine developed by the Dominion Coal Co.; heavy duty flexible type scraper chain conveyors for transporting the coal from the longwall face; diesel haulage locomotives; one colliery installed a cable belt conveyor, the first of its kind on the continent. Finally, improved haulage equipment and the expanding use of improved roof bolting methods have helped to increase production per man shift.

In an attempt to recapture some of the domestic heating market, the Dominion Coal Co. developed the Dosco Downdraft furnace. Large scale performance tests were conducted last winter with this furnace and with conventional oil fired furnaces in order to compare general acceptance. Only preliminary reports on the results have been received, consequently no comments can be offered.

Some interest has been shown in the domestic crossfeed stoker for both anthracite and bituminous coals. It is simple in design and amenable to automatic coal feed and ash disposal which are essential features to compete with other fuels. However, with ample natural gas and oil available at low cost it is not expected that any coal burning equipment will compete successfully.

In the commercial field, the packaged coal fired boiler of 3000 to 60000 E.D.R. capacity, being promoted by the Bituminous Coal Institute in the U.S.A., is expected to find many applications in Canada and it is hoped that this type of boiler can help to retain the important commercial class of market for coal in Canada. The vibrating or oscillating grate with spreader coal feed is gradually emerging and may be successful in displacing the travelling grate in many commercial and small industrial boilers because of simplicity of design, lower cost and flexibility. Furthermore, the design lends itself to water cooling, if necessary.

The 'turbo furnace', a recent development of the Riley Stoker Corpn in the U.S.A., has features which appear to suit many Canadian coals. None have been installed in Canada but the design may find a place in the expanding thermal power generating industry.

Technical and scientific meetings

1957—Two meetings held in Canada during 1957 may be of interest and were briefly reported last year [*Fuel, Lond.* 36 (1957) 116]. Further details can now be given.

(*1*) The Sixth Commonwealth Mining and Metallurgical Congress (erroneously reported last year as the Seventh Congress) commenced on 8 September in Vancouver and terminated on 9 October in Halifax. A comprehensive symposium has been printed and is entitled *Mining in Canada*. The volume is available from the Northern Miner Press Ltd, 116 Richmond Street West, Toronto at a cost of $10.00.

(*2*) The A.S.M.E.–A.I.M.E. Twentieth Annual Joint Solid Fuels Conference was held in Canada in conjunction with the Coal Division of the Canadian Institute of Mining and Metallurgy. This American National Conference was held outside the U.S.A. this year for the first time and took place in Quebec on 10 and 11 October.

1958—The only large meeting of interest which is now known to be planned for 1958 is the Annual Meeting of the Canadian Institute of Mining and Metallurgy. The dates have not been settled but it will automatically be held in Western Canada.

Dr H. D. SMITH of the Nova Scotia Research Foundation states that there are no plans to hold a conference during 1958 in Canada on the origin and constitution of coal similar to that which was held in Nova Scotia in 1956. We have recently been advised that the Mining Society of Nova Scotia plans to hold a Coal Research Conference at Keltic Lodge on 3, 4 and 5 July 1958. All enquiries concerning this Conference should be addressed to Mr S. C. MIFFLEN.

GERMANY

An abridged report of a study tour made in 1956 by L. SIMONSSON, of The Royal Swedish Academy of Engineering Sciences, and O. STENBERG, of Stenbergs Maskinbyrå, Stockholm, is included through the collaboration of Dr W. GUMZ.

Among the German public institutions for technical scientific research there are about twenty dealing with fuel and heating techniques which between them pretty well cover the field. Research and development work in respect of fuel technique is moreover carried on by industrial establishments.

With some few exceptions the independent research institutes are comparatively small. Consequently developments in fuel technique are mostly due to industrial establishments. There are several important undertakings in the field that have particularly large research resources. This applies likewise to such industrial cooperative bodies for fuel technique development work as Steinkohlenbergbauverein and its affiliated organization Gesellschaft für Kohlentechnik m.b.H., Ruhrkohlenberatung G.m.b.H. and Vereinigung der Grosskesselbesitzer e.V.

The following constitutes an account of present work (spring 1956) in the fields concerned.

XUM

(1) *Coal and coke*

As we know, German energy supplies are for the most part based on coal and brown coal or lignite from domestic deposits. The outstanding position of coal leads to a large part of research and development being devoted to that fuel. For the carrying out of the research and experimental work, Steinkohlenbergbauvererin has its own laboratories in Essen and Dortmund. To a large extent the resources of affiliated mining companies as also of independent research institutions are utilized as well.

Work in the field of chemistry is done at the research organization Gesellschaft für Kohlentechnik m.b.H. This company's main laboratory at Dortmund-Eving was expected to be transferred to the new central research institute at Essen-Kray before the end of 1957.

Extensive work is being done with the object of increasing production, chiefly of course by mechanization of mining operations, and to ensure better working conditions for the mineworkers.

Optimism is apparent regarding the possibility of maintaining coke production, though coke consumption is estimated to rise considerably in the near future. The coke problem is treated both by mining technique measures and by development of methods for coal sorting, mixing and precoking. Trials are being made with eking out the coking coal proper by mixing in other sorts of coal. Coal slack, which has too high an ash content for coke manufacture, can be concentrated by flotation. Competition from the oil industry means that the coal industry must devote itself to measures for improving quality more than ever before.

Very extensive work is also done with a view to increasing gas production both by rationalization of the conventional gas and coke works and by the adoption of new methods for total gasification. Special gasifying methods are being worked out also to enable low value fuels such as coal slack, washery refuse and oil shales to be utilized. For the gasification of washery refuse, *Waschberge*, an ash-rich waste from the coalmines, with a calorific value of 1000 to 2000 kcal/kg, and oil shales, methods are being developed by the firms of Dr C. Otto and Lurgi Gesellschaft für Wärmetechnik.

Ruhrgas A.G. has developed a method of gasification of inferior coal in a vertical cyclone chamber. The pulverized coal is introduced, together with pre-heated air, through a number of nozzles located tangentially in the lower part of a high vertical cylinder. The gas produced has a calorific value of about 800 kcal/Nm³ and is specially intended for the under-firing of coke retorts. A full size plant has recently been put into operation at Recklinghausen.

For the gasification and devolatilization of inferior coking coal Lurgi and Ruhrgas A.G. have a pilot plant in which pyrolysis is obtained by mixing the coal with recirculated fine-sized coke dust. The coke circulates between a gasification chamber and a combustion chamber where heating is obtained by combustion with pre-heated air. The coarser coke pieces are separated in a cyclone separator above the combustion chamber from the hot dust-containing flue gases which are conveyed to a steam boiler. Coking by this method is considered to be of importance for the recovery of gas from coal

used as fuel in steam power stations; and a weakly caking coal can be used without causing trouble.

For the production of town gas (domestic gas) from a non-coking weakly caking coal, there was put into operation at Dorsten a total gasification plant working on a pressure gasification principle developed as a common research project by Lurgi and Ruhrgas A.G. The plant has been constructed for a production of 1·5 million Nm^3 gas per day. Gasification is done by oxygen gas supplied by a Linde plant.

Other phases of development of present interest in the gas field are underground storage of gas and the production of gas from oil.

In the chemical sector of the German coal industry's research activities, work is proceeding on the refinement of tar compounds and the conversion of coal to chemical products. The raw chemicals produced from the coal tar were formerly dealt with solely by the chemical industry, but marketing difficulties and low prices have led to the coal industry interesting itself in treating these products to an increasing extent.

Methods have been developed by the Gesellschaft für Kohlentechnik m.b.H. for the production of active carbon and electrode carbon from German coal. For both these products there is required coal of very low ash content, less than 0·5 per cent which is obtained by a special flotation procedure.

A separate committee in the Gesellschaft für Kohlentechnik m.b.H. is dealing with questions concerning the structure of coal and is collaborating for this purpose with the Institut für Spektrochemie und Angewandte Spektroskopie in Dortmund-Aplerbeck.

Research with no restriction of aims in the field of coal chemistry is being carried on at the Max-Planck-Institut für Kohlenforschung at Mülheim. In recent years this institute, owing to income derived from its own patents has acquired a substantially augmented financial basis for its work. The equipment of the institute is excellent.

Coal research in conjunction with fuel problems has been entirely abandoned at the institute. For several years the work has been specially devoted to the chemistry of metal alkyl compounds. The result of this fundamental scientific work has led to undreamt of results in the field of applied chemistry. The methods for the polymerization of ethylene by means of aluminium alkyls and other metal organic compounds have become particularly well known.

A comparatively new research institute for fuel technique is the Carl Engler- und Hans Bunte-Institut für Mineralöl- und Kohleforschung established in conjunction with the Technical College at Karlsruhe. Special attention has been devoted to the nitrogen-containing compounds in coal, and comparative experiments have been performed with brown coal and peat. Further, the thermal conditions in coking processes have been studied, as well as the difference between various coal fuels in gasification respects and wet methods of coal cleaning. Chromatographic separation has been employed for investigation of the constituent parts of coal tar and peat tar.

XUM

A great deal of work in Germany is devoted to developments in combustion technology. One important question has been to meet the increased demand for operating reliability arising with the adoption of very large boiler units. A significant part of the work in this field is carried out by Vereinigung der Grosskesselbesitzer e.V.

The problem of firing with coal containing much ash has been solved by the adoption of slagging furnaces. It has been possible progressively to increase the efficiency of these and they can now be run with the same efficiency as grates fired with high class coal. About 60 per cent of new boiler plants built in Germany are equipped for firing with pulverized coal and slag tapping (*Schmelzfeuerung*).

Investigation in recent years has substantially increased knowledge of how fouling of the heating surfaces takes place. It has been found that sublimated and re-oxidized silicon dioxide contributes largely to the deposit formation. The tube surfaces, when oxidized, show a needle-like formation of iron oxide and promote the adhesion of solid particles. By means of adaptation of the combustion conditions and the de-sooting procedure (shot cleaning) success has been achieved in very considerably lengthening the interval between laying off the boilers.

(2) *Oil*

Domestic extraction of mineral oil in Germany has increased appreciably in the last few years, and in 1955 it was no less than 3·15 million tons.

Among institutes in the service of the oil industry is Institut für Erdölforschung at the Technical College in Hannover. The institute has fairly spacious laboratories for chemical and physical investigations. Besides work in the chemical field, a technique has been developed at the institute for sampling crude oil in deep drill holes and investigation of these samples in such a way that the pressure prevailing at the place of sampling is maintained throughout.

(3) *Gas*

The employment of gaseous fuel for industrial and domestic purposes has increased rapidly in Germany in recent years. The total annual production in 1954 was almost 35×10^9 Nm^3.

The extensive work that is proceeding to develop methods for the production of gas from solid and liquid fuels and for the purification of gas and for gas transport, is done for the most part by the large industrial undertakings previously mentioned.

For the treatment of questions connected with the employment of the gas as a fuel there are two institutes, namely Gaswärme-Institut in Essen and Gas-Institut der Technischen Hochschule Karlsruhe. The former is fairly well equipped. Among other things, it has its own gasworks for the production of generator gas and water gas. The working programme is on practical lines and consists for the most part of improving efficiency and operating reliability as also the quality of heat treatment with the employment of gaseous fuels.

The latter is a college institute. It has separate departments for investigations in the fields of chemistry, employment of gas and water. Among the tasks of the institute is the testing of apparatus for interconnection in public gas systems.

(4) *Peat*

There is a government institute at Hannover for research in the peat field, Torfinstitut. Work here is largely directed to problems connected with the up-grading of black peat, including the treatment of the peat for forming pieces suitable for drying, briquetting and the production of peat coke.

For field experiments there is Torfforschung G.m.b.H. at Bad Zwischenahn, which comes under the Torfinstitut. Among other things, they are engaged on developing methods for automatic stoking with peat.

(5) *Electroheating*

There are two institutes for electroheating in Germany, viz. the Elektrowärme-Institut with laboratories at Langenberg/Rhld and Essen, and the Institut für Elektrowärme an der Technischen Hochschule Hannover. The former has a department for industrial heating at Langenberg, and a department for domestic heating at Essen.

The work of the industrial heating department lies largely in the field of high frequency heating. In the laboratory for domestic apparatus there are good facilities for the testing of refrigerators, cooking ranges, hot plates and the like. There is also a test bakery.

The Institut für Elektrowärme at Hannover is quite small. The work includes investigations of the properties of resistance wires and insulating material, the study of heat transmission by convection and radiation, radiation properties of materials, etc.

INDIA

In his latest report Dr J. W. WHITAKER states that during the past year much thought has been given to assessing the fuel requirements, and energy requirements in general, that are likely to arise with the development of the successive five year plans of increased industrialization. As a first step the output of coal is to be raised from the existing amount of 40×10^6 to 60×10^6 tons per annum by 1960. The output of ingot steel is to be raised to 6×10^6 tons from the existing amount of $1{\cdot}5 \times 10^6$ tons per annum.

Steel

At present, new steelworks are being established at Rourkela (Orissa), Bhilai (M.P.), and Durgapur (West Bengal), and the existing steelworks at Jamshedpur and Burnpur are to double their outputs. There will thus soon be five major steelworks. The amount of high grade coking coal required by them will be of the order of 10×10^6 tons a year, as against the existing consumption of nearly 3×10^6 tons. Much of this new coal will be washed coal, and the establishment of the necessary washeries has been taken up. They will be located at: (*a*) Kargali (West Bokaro Field), (*b*) Dughda (Jharia field), and (*c*) Durgapur (West Bengal). Central washeries are being favoured

XUM

(of capacity between 1 and 2 $\times$ 10^6 tons per annum), but individual washeries on a smaller scale may be adopted to some extent. Generally speaking, combinations of heavy medium and of jig washers are proposed. Of the three existing washeries, two are of the heavy medium type (Chance cone), while the third is a jig washer (Acco type) with feldspar bed.

As an indication of the proposed production of iron and steel contemplated in *subsequent* years, the estimate for 1965 is some 15 $\times$ 10^6 tons of steel and 2 $\times$ 10^6 tons of pig iron, roughly the present production of the U.K. By 1975 it is intended to double these quantities. For this production (1975) about 80 $\times$ 10^6 tons of raw coal will be mined: most of it will be washed, giving a yield of perhaps 55 to 60 $\times$ 10^6 tons of washed coal for coking.

By 1975, the overall coal requirement for the country will be 320 $\times$ 10^6 tons, i.e. roughly four times the raw coal to be mined for the steelworks.

Regarding domestic fuel, a consumption of about 40 or 50 $\times$ 10^6 tons is forecast, all of which will be carbonized at low temperatures in by-product plant giving a considerable yield of coal tar oils, benzol, etc.

The coal consumption for thermal power is forecast at 50 $\times$ 10^6 tons per annum for 1975; and for the cement, refractories, potteries, glass and brick industries, the present amount of about 6 $\times$ 10^6 tons per annum is expected to be increased tenfold and thus to approach 60 $\times$ 10^6 tons.

Regarding rail traction, the present consumption is about 12·5 $\times$ 10^6 tons per annum. If steam transport alone were to be adopted, the forecast increase would be some eightfold, bringing the railway coal consumption to no less than 100 $\times$ 10^6 tons. Electrification and dieselization, however, are already being introduced, and the coal consumption of the railways is expected to approach only 50 or 60 $\times$ 10^6 tons, depending upon the form of traction and the extent to which it is adopted.

These total requirements at a little over 300 $\times$ 10^6 tons per annum represent an eightfold increase over present day output. Even so, the coal consumption per head will be far less than one ton per annum, as against five for the U.K. at present.

Oil and natural gas

Regarding mineral oil products, the present consumption is very close to 4 $\times$ 10^6 tons per annum, of which 90 per cent is imported. It is expected to increase the home production to no less than 40 $\times$ 10^6 tons per annum by 1975, but these developments will depend largely on the success of the present borings for petroleum. Some oil, however, will also be got by treatment (hydrogenation) of the low temperature carbonization oils, and perhaps also by Fischer–Tropsch synthesis following low grade coal gasification.

For exploration and prospecting for petroleum, the Government of India has established a Natural Gas and Oil Commission, and already extensive borings are being made. The Assam Oil Co.'s discovery of a valuable oil reserve in the Naharkatia area (Assam) has led to proposals for a further refinery. This area is likely to yield at least 2·5 $\times$ 10^6 tons of oil products per annum in the near future. The present output from Digboi is only about 0·5 $\times$ 10^6 tons.

Lignite

The above data refer mainly to bituminous coal and petroleum. It must also be said that active steps are now being taken to develop the lignite deposits at South Arcot, Madras. Some of the lignite will be used untreated for power production, some will be processed for briquets, carbonization, and fertilizer manufacture. It is proposed to increase the lignite output to 7×10^6 tons per annum by 1965. There are also under consideration schemes for gas grids for West Bengal and Calcutta (to be supplied from the carbonization plant at Durgapur), and for Madras to be supplied from lignite gasification at South Arcot (Neyveli).

Recent borings in the (main) Raniganj and Jharia coalfields, and in other (minor) coalfields, have shown that the country's assets both of coking and of non-coking coal are many times greater than was thought five years ago.

The picture therefore is one of great activity in all forms of fuel production.

Scientific research

Regarding scientific investigations and research, an important symposium on coal carbonization held at the Fuel Research Institute, Jealgora, in February 1957, was attended by leading fuel technologists not only from India, but also from the U.K., Germany, Japan and Russia.

Progress has been made and standard specifications issued by the Indian Standards Institution for the sampling and testing of coal and coke. A comprehensive scheme for coal classification and nomenclature has also been drawn up by the same body. Most of the coals of India are drift coals and perhaps for this reason are amenable in the main to systematic classification in spite of their fairly high content of mineral matter.

Successes have also been achieved in the use of additions of low temperature char (in pilot plant work) in making strong coke from relatively weakly caking coal. Recently a modified chain grate stoker, enclosed in a firebrick furnace and operated with reduced primary and secondary air, has been shown to be capable of producing excellent semi-coke for domestic purposes, and at the same time surplus heat is available.

The coal survey work, which is conducted by regional laboratories as in the U.K., has been continued and intensified: these laboratories have given valuable help in the assessment of the quantity and quality of coals available in the different coalfields, in the analyses and tests of borehole samples, in washability assessment, and so forth.

Mining research

With the increased activity in coal mining and in the mineral development of the country, a Mining Research Station is being set up at Dhanbad, Bihar. The plans have been approved and the construction is now in hand. The station will deal with the problems of mining not only coal (which is the most valuable mineral product of the country) but also ore and stone. In respect of coal a major mining problem in India is how to obtain optimum extraction from thick seams. The main coal seams of the country are from 10 ft to 100 ft thick. It is not usual to regard seams below 4 ft in thickness as worthy of attention! Nevertheless, to obtain maximum yield with safety from seams which

XUM

are, say, 20 ft or 30 ft in thickness presents considerable difficulties. In the past much coal has been lost because of spontaneous combustion, collapse of pillars, and even from the very necessity to leave adequate coal pillars of reasonable strength. It is true that extensive stowing, especially sand-stowing, has been adopted with success in some mines, and valuable experience in this field has been gained. Much, however, remains to be done by way of investigation and research, and a considerable section of the work of the Mining Research Station will be concerned with improvements in efficiency, studies of strata stresses, roof control, stowing, mechanization, alternative methods of mining, and the like.

The objectives of the station as a whole are manifold, but they may be briefly summarized as 'the improvement of safety, of health, and of efficiency in mining'. In view of the developments proposed in the exploitation of the mineral wealth of the country, the establishment of such a station is opportune.

JAPAN

Dr AKIRA SHIMOMURA reports that the Committee for Promoting Utilization of Low Grade Coal was launched in October 1956 by the sponsorship of the Japan Power Association, and has investigated the possibility of developing the gasification industry in Japan.

Carbonization in the fluidized state has been studied by the Resources Research Institute and the Coal Research Institute, and successful pilot plants have been developed.

Japan's largest gasworks, the Toyosu Works of the Tokyo Gas Co., was completed toward the end of 1956, which adopted GI complete gasification plant in addition to conventional coke ovens, and gas purification under pressure.

Dry natural gas is being sought by many ammonia and methanol manufacturing companies, and domestic use of bottled LPG has very much increased.

The Atomic Energy Research Institute started its experimental reactor of water-boiler type toward the end of August 1957.

The Fuel Society and other technical societies and associations are active in holding meetings and giving lectures on fuel matters, and several papers on fuel and electric power have been submitted to such international conferences as ECAFE II. Mineral Products Development Sub-Committee (held in Tokyo, June 1956), Fifth World Power Conference, Sixth International Combustion Conference, etc.

During the last year, Dr W. REERINK (Germany) and Dr W. J. PODBIELNIAK (U.S.A.) visited Japan and delivered lectures.

THE NETHERLANDS

Caltex Central Laboratories

The increasing complexity of product application problems, especially as they may affect the Caltex Group's refining and marketing operations, has

suggested the need of a centrally located analytical and research establishment To this end the Caltex Central Laboratories are now under construction on a site of about eight acres at Pernis, near Rotterdam [*Oil Progr.* (3 July 1957) 7].

The laboratories are being constructed in stages with as little delay as possible, with completion scheduled for mid-1958, when it is expected that about 70 chemists and technicians will form its operating staff.

The laboratories will be equipped with catalytic processing equipment, bench scale distillation and thermal conductivity type low temperature fractional distillation apparatus for the analysis of hydrocarbon gases, a chromatographic analyser for petroleum fractions, and apparatus for testing under actual operating conditions such equipment as kerosene-operated refrigerators and chicken-incubators.

The construction schedule also calls for the completion, in mid-1958, of a chassis dynamometer installation, six large engine test cells and one small one, an engine overhaul and inspection shop and the many ancillary buildings and equipment needed.

The chassis dynamometer, which is one of the major functional units of Caltex Central Laboratories, is an apparatus for testing and measuring vehicle performance under simulated road conditions. What makes the chassis dynamometer unique is that it will be able to handle every size of car, and gauge its performance and fuel consumption under any ambient temperature from — 30 to 120°F at road speeds up to 100 miles per hour.

The Caltex Research and Development group will be in a position adequately to render technical service where required on the many and varied technical problems which arise in product application and refinery processing.

Second International Conference on Coal Science, 1957

The Second International Conference on Coal Science was held at Valkenburg from 1 to 4 May 1957. Like the previous Conference held at Heerlen in 1955, it was organized by an international Committee comprising Prof. D. W. van Krevelen, Geleen (president); Dr I. G. C. Dryden, Leatherhead; Prof. W. Fuchs, Aachen; Ir E. H. Grand'ry, Tertre; Ir R. Loison, Verneuil; Dr M. T. Mackowsky, Essen; Dr D. C. Rhys Jones, Cheltenham. The Conference was divided into four Symposia dealing with: (*a*) Chemical methods of coal research, chairman Ir Grand'ry; (*b*) New physical techniques in coal research, chairman Dr M. T. Mackowsky; (*c*) Physicochemical studies of coal macerals, chairmen Dr I. G. C. Dryden and Prof. W. Fuchs; and (*d*) Fundamentals of coal carbonization, chairmen Ir Loison and Dr D. C. Rhys Jones.

Some 150 coal scientists from ten countries attended the Conference. The U.S.A. (both Government and industry) was directly represented for the first time. The Polish delegation was headed by Prof. B. Roga of Glownego Instytutu Gornictwa, Katowice, and the Yugoslavian one by Prof. Maks Samec, Director of the Kemični Institut 'Boris Kidriča', Ljubljana, who was at the same time official delegate of the Slovene Academy of Arts and Sciences.

The meetings themselves were characterized by animated discussions on the papers which had been distributed as preprints, the presentation itself

XUM

being limited to 15 minutes. It was generally felt that since the previous conference notable advances had been made in the various techniques of coal investigation, especially on the composition and properties of the pure coal macerals and that the advance was particularly important as regards physical techniques.

An interesting item in the programme was a colour film on the behaviour of certain coal constituents on heating thin sections under the microscope, which was made by Prof. W. Spackman, Dr W. F. Berry of Pennsylvania State University and Mr A. H. Brisse of the United States Steel Corporation and sent on loan by Prof. Spackman.

At the end of the Conference, when the results were summarized by Prof. van Krevelen, it was generally agreed by both organizers and audience that a third Conference should be organized in two years time and be held again in the Netherlands.

The proceedings of the Conference, i.e. papers with discussions, will be published as a special issue of *Brennstoff-Chemie*. The participants at the Conference will receive a free copy of the issue.

The foregoing notes on activities in the Netherlands were kindly supplied by Prof. H. I. Waterman and Prof. D. W. van Krevelen (see also page 90).

Publications

TASCHENBUCH FÜR DAS GAS- AND WASSERFACH
Teil II: GAS [Gas Pocketbook]

Munich: R. Oldenbourg, 1957. $x + 314$ *pp.* *DM* 16.00

THIS handsome little book briefly summarizes all the processes of gas manufacture and purification. The references are almost exclusively confined to German literature.

Section I deals with the planning and building of gas works, selection of the oven system, transport of coal and coke, steam power and water supplies, gas holders, meters, governors and distribution.

Section II covers types of coal and carbonizing plant. The subject matter on continuous vertical retorts and horizontal retorts is rather meagre as these types of plant are not common in Germany.

Section III outlines gasification processes including producer gas, Doppel gas and the Lurgi process.

Section IV deals briefly with refractories.

Section V, which is the best section of the book covers gas treatment including condensation, governing, gas exhausters, secondary coolers, tar removal, naphthalene ammonia and cyanogen washing, sulphur removal, benzole recovery, detoxification, gas drying, nitric oxide removal and intensive cooling.

Section VI deals with the handling and treatment of the by-products, coke, tar, benzole, sulphur, cyanogen and ammonia.

Section VII covers laboratory investigations such as coal analyses, coke testing, examination of bog ore and spent oxide, water analyses, tar analyses, and benzole analysis.

Finally the book deals with gas distribution, gas testing, metering and pressure regulation.

It is felt that the book provides a useful introduction to gas works practice for junior technicians.

S. PEXTON

PRÁCE ÚSTAVU PRO VÝZKUM A VYUŽITI PALIV
[COMMUNICATIONS OF THE INSTITUTE FOR RESEARCH ON AND UTILIZATION OF FUELS]

Prague: Czechoslovak Ministry of Fuels, 1957. Vol. VIII, 223 *pp*; Vol. IX, 210 *pp*

THESE two volumes contain the latest thirteen of the 28 or 29 papers which have been published in this form since 1954. The papers are in Czech, with abstracts in English (as well as in Russian and in German); the following remarks are perforce based on the abstracts. In Volume VIII J. Šnable reports experiments on diffusion of gases in mine air; V. Procházka describes a process for obtaining pure methane from natural gas, using active charcoal, metallic calcium and repeated condensation and evaporation; Procházka also describes the determination of gases physically fixed in coal by an improvement in the method of Peters and Warnecke; J. Koštál reports on the solvent extraction of Czechoslovak coals under hydrogen pressure; B. Tejnický describes coking trials on blends containing weakly caking Czechoslovak coals and a laboratory method for the prediction of coke quality from a sample of coal; V. Bortlik records experiments on the effects of ash, humic substances and bitumen on the water resistance of briquettes; and F. M. Kessler describes methods of determining titanium and magnesium in coal ash. In Volume IX there are papers by J. Novák and F. Sünderhauf on the combustion of fines and low grade fuels on chain grates; and by Č. Lipka on the determination of fuel consumption in power stations.

XUM

THE MINISTRY OF POWER STATISTICAL DIGEST, 1956

London: H.M. Stationery Office, 1957. *xii* + 216 *pp.* 150 *tables*, 4 *maps.* 37*s* 6*d*

FROM year to year this Journal tables note of the British Ministry of Power's *Digest* of the statistics relating to coal, petroleum, hydroelectric power and the secondary fuels and power (coke, gas, thermal electric power etc.). This volume gives similar tables to those of recent years somewhat more detailed and complete. It is pointed out in the Introduction that special tables were included in 1952 for consumption of solid fuels and black oils in the various industrial and non-industrial undertakings, in 1953 the survey of steam and power utilization in industrial and commercial undertakings and in 1954 a detailed geographical survey of fuel consumption in connection with the air pollution inquiry. This year there is no special survey, but reference is made to the statistical material provided in the reports of the National Coal Board, the Gas Council and Gas Boards and the Electricity Boards. Although detail is provided as to the consumption of electrical energy for domestic, farm, transport, industrial and other users, it is still difficult to assess from the information in the Tables the amount of energy provided for the production of mechanical power, processing and warmth. It is important to have a measure of the electrical and mechanical power per worker, and to know the rate at which this is augmenting. It would also be helpful if tables could be provided which would give information as to the improvement in efficiency in the use of fuels for process needs, as well as for domestic purposes.

Inland consumption of coal (adjusted) is given for 1956 as 214·5 million tons and 253·7 together with oil and hydroelectricity (on an equivalent coal basis). This seems to be rising at almost 4 millions tons per annum, but mainly because of the increased consumption of oil. It will be good when some day the *Digest* shows brighter statistics for coal production; the tables relating to accidents in mines, however, are cheering. The average thermal efficiency of generating stations and the electricity generated per ton of fuel is steadily rising (Table 87).

The capital expenditure of the gas industry (Table 121) is almost a quarter of that of the electricity undertakings (Table 102), and the latter figures may be higher in future *Digests*, as the nuclear power station programme takes shape. Particularly interesting are the tables relating to petroleum (28·643 million tons was imported). Table 138 shows that in 1955 the output of refined products was 25·667 million tons. It is impossible in a short review to refer to all the interesting tables which altogether number 150, but the *Digest* is essential for those who need to keep watch on the production and use of Fuel and Power in Great Britain.

A. C. EGERTON

Letters to the Editor

Letters to the Editor on points of scientific interest related to fuel science are invited. The Editor does not hold himself responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.

Briquetting of British Lignite without Binder

IN ITS texture the British Devonshire lignite resembles the Czech brown coal from the north of Bohemia. On a commercial scale the British lignite is briquetted using up to 10 per cent of the binder, while the Czech brown coal from northern Bohemia is currently being briquetted without binder after a thermal treatment. Therefore it may be of interest to British workers in this field to be informed very briefly of the method of briquetting British lignite without binder used in experiments carried out in Czechoslovakia in 1948.

The briquetting without binder is successful only after a thermal pre-treatment of the lignite. This heat treatment or 'activation' is based on the generation or forcing of the tar *in statu nascendi* from coal particles to their surface where it condenses or is 'stabilized'. The activation takes place at temperatures above 840°F, the stabilization at 170° to 300°F. In large scale production, the heat treatment is carried out in a drying oven working on

Table 1

Sample No.	*A–174*	*B–175*	*C–176*
Lignite analysis:			
Moisture, per cent	31·72	32·10	30·15
Ash, per cent	7·48	8·11	8·77
Extract by benzene, per cent	1·91	2·13	1·97
Tar, total, per cent	7·39	7·95	8·89
Activation temperature, °F	1382	1202	1058
Briquetted coal:			
Moisture, per cent	11·89	14·50	14·10
Grain size	*Normal* (c. 19 *per cent through mesh* 230)		
Briquettes:			
Compressive strength, lb/in²	2382	2796	2306
Breaking strength, lb/in²	230	240	252
Friability, per cent	71·0	72·0	59·4
Water absorption (by immersion)	*No change*	*No change*	*No change*

the principle of a Lurgi oven. The coal is protected against oxidation either by a medium of combustion gases produced by burning water gas, or by carbon dioxide. The treated coal is then briquetted at 170° to 180°F in a ring-roll press at a pressure of 35·550 lb/in².

Altogether, three small samples of British lignite were treated and briquetted on a laboratory scale. The results are summarized in *Table 1.*

XUM

For the sake of comparison, two briquetting experiments were carried out with lignite which had not been thermally treated and in which two per cent of the binder (pitch) was used. Results obtained were completely unsatisfactory. A more detailed report, including the discussion of the theory of this process, can be found elsewhere[1].

V. VČELÁK

Ministry of Fuel,
Prague,
Czechoslovakia

(*Received June 1956*)

REFERENCE

[1] VČELÁK, V. *Braunkohle Wärme Energie* 9 (No. 9/10) (1957) 187

Fine Grinding of Coal and Coke for Special Analyses

THE analysis of coal and coke is usually carried out on material which has been ground so that at least 99 per cent passes 72 mesh*, but for certain

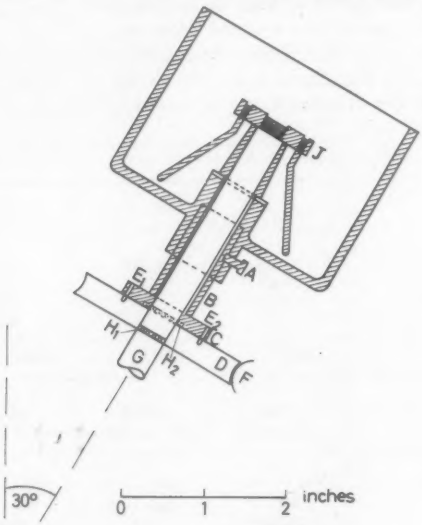

Figure 1. Section through centre of laboratory mill for fine grinding of coal and coke

purposes it is desirable to use material ground so that at least 99 per cent passes 240 mesh. Three such purposes are the determinations of pyritic sulphur in coal[2], sulphide sulphur in coke[2] and nitrogen in coke[3]. It is laborious to grind by hand the analysis sample (through 72 mesh) to through

* All sieve sizes mentioned in this paper refer to British Standard test sieves[1].

240 mesh and a small laboratory mill has been devised for this purpose. The mill and its performance are described in this letter.

The mill, illustrated in *Figure 1*, consists of a bronze* cup 3 in. in diameter and $2\frac{1}{4}$ in. deep, containing 120 ball bearings of $\frac{1}{4}$ in. diameter. It is secured by a pin, A, to a brass sleeve, B, which forms part of a bush C, the bush being attached to the driving gear, D, by means of 2 screws, E_1 and E_2. D is rotated at about 140 rev/min by a worm drive, F, and an electric motor of 1·3 lb in. torque. A central, fixed shaft, G, at an angle of 30° to the vertical, passes through the unit, smooth rotation of the cup being ensured by the ball-races H_1 and H_2. To the shaft G is threaded a unit, J, which has two bronze wires screwed into it to impart a tumbling motion to the balls. A cover glass is secured on the top of the cup by a rubber band.

A charge of 10g of coal or soft gas coke, through 72 mesh, is ground to 100 per cent through 240 mesh in 30 min (*Figure 2*). A similar charge of a

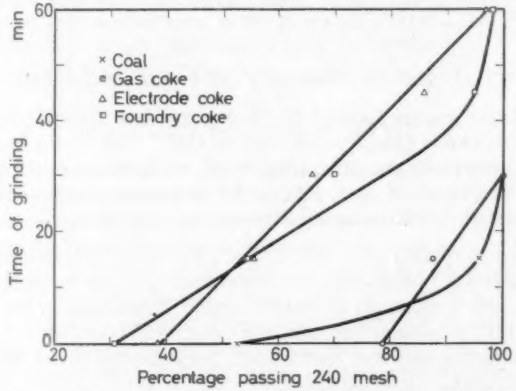

Figure 2. Fine grinding of coal and coke in the laboratory mill

hard foundry or electrode coke requires approximately 60 min. In general, the time required increases with the hardness of the material and is proportional to the percentage of over-240-mesh material in the through-72-mesh feed.

When grinding coke for the determination of sulphide sulphur, it is desirable, since ferrous sulphide is liable to oxidation when the surface area per unit weight is increased, to add 5 ml of alcohol and, in effect, to grind as a paste. After the required period of grinding, the balls are separated from the charge by sieving with an $\frac{1}{8}$ in. sieve and the product dried for 20 min at 90°C, the caked material then being dispersed by grinding for a few minutes in an agate mortar.

When grinding 10 g of electrode coke for 60 min, it was found that the ash increased by 0·5 per cent; contamination to this extent is unimportant for the purposes for which the mill has been used.

* The cup for the prototype mill was machined from a bar of sand-cast bronze composed of Cu 90, Sn 10 per cent. Though this proved to be satisfactory, it would be preferable to use rolled bar (which is less liable to contain blow-holes) of, e.g., aluminium bronze made to *B.S. 2032*[4].

The author wishes to acknowledge the assistance of Mr E. Jillings in the design of the mill. The work formed part of the programme of the British Coke Research Association, to whom the author is indebted for permission to publish.

H. C. WILKINSON

British Coke Research Association,
74, Grosvenor Street,
London, W.1

(*Received May 1957*)

REFERENCES

[1] *Test sieves, B.S. 410* British Standards Institution: London, 1943
[2] RADMACHER, W. and MOHRHAUER, P. *Glückauf* 89 (1953) 503
[3] MOTT, R. A. and WILKINSON, H. C. To be published
[4] *Aluminium bronze rods, sections and forgings for general engineering purposes, B.S. 2032* British Standards Institution: London, 1953

The Contact Angle of Mercury at Coal and Char Surfaces

IN A recent letter in this Journal O. G. INGLES[1] has derived values for the contact angle between mercury and coal or char. The values found by him differ appreciably from the value used by H. L. RITTER and L. C. DRAKE[2], P. ZWIETERING and D. W. VAN KREVELEN[3] and others in the determination of the pore size distribution in coals by the mercury penetration method.

The derivation of the pore size distribution from measurements of the mercury penetration is based on the assumption that all the pores are cylindrical. Although a spectrum of radii is found, Ingles uses in his calculation of cos θ the further assumption that the cylindrical pores all have the same radius r. Dropping this last assumption the relations given by Ingles are modified as follows.

The pressure P_1 required to force mercury through a packed plug of coal will be determined by the radius r_1 of the largest cylindrical pores according to $P_1=2\gamma_1 \cos\theta/r_1$, but the pressure P_2 needed to prevent penetration of a completely wetting liquid in the same plug is determined by the radius r_2 of the smallest pores according to $P_2=2\gamma_2/r_2$, whence $\cos\theta=r_1P_1\gamma_2/r_2P_2\gamma_1$ (γ_1 and γ_2 being the surface tensions of mercury and the wetting liquid respectively). Putting r_1 equal to r_2 Ingles calculates too low values for cos θ. The discrepancy between his values and the values used by Ritter, Drake and others may be explained by values of r_1/r_2 lying between 1·3 and 5.

We further remark that in this special case, where a plug, made by compressing coal powder, is used, the model of cylindrical pores seems very unrealistic. A packing of spheres would be a more realistic model. Starting from the calculation by L. V. RADUSHKEVICH[4] of the capillary condensation around the point of contact of two isolated spheres we have calculated the capillary condensation and the mercury penetration in packings of spheres. These calculations, which will be published in the near future, predict that

the mercury will be forced out of the packing at a lower pressure than that at which it is forced in. In preliminary experiments with a plug of glass spheres this prediction was verified. This means that in a plug made by compressing more or less spherical particles mercury penetration will show hysteresis apart from the difference between the advancing and the receding angle of contact.

S. KRUYER
D. W. VAN KREVELEN

Central Laboratory,
Staatsmijnen in Limburg,
Geleen, The Netherlands

(*Received June 1957*)

REFERENCES

[1] INGLES, O. G. *Fuel, Lond.* 38 (1957) 253
[2] RITTER, H. L. and DRAKE, L. C. *Industr. Engng Chem. (Anal.)* 17 (1945) 787
[3] ZWIETERING, P. and VAN KREVELEN, D. W. *Fuel, Lond.* 33 (1954) 331
[4] RADUSHKEVICH, L. V. *Izvest. Akad. Nauk S.S.S.R.* (1952) 1008

Systematics of High Volatile Coals

IN ANY system of classification the high volatile coals (containing more than 35 per cent on the unit coal basis) and the high moisture coals (more than 2·0 per cent air-dried moisture) present difficulties. In all recognized systems of classification based essentially on proximate analysis (such as those of M. GOUTAL[1], S. W. PARR[2], R. A. MOTT[3] or the A.S.T.M.[4]) special provision has been made for these problem coals. Even in C. A. SEYLER'S[5] coal chart, based on elementary analysis, these coals stand out in sharp contrast by their exclusive position in the horizontal part, demarcated roughly by the 85 per cent carbon line. B. K. MAZUMDAR[6] and collaborators have pointed out recently that the unique character and properties of high volatile coals are essentially due to their similar structural pattern in contradistinction to that of the high rank coals.

Viewed against this structural background, the new systematics of coal[7] which the author has been developing for some years appear to throw further light on the behaviour and constitution of high volatile coals. It was shown that for any successful classification of such coals, from proximate analysis alone, not *only the quantity but also the quality* of the volatiles is an important parameter. The 'quality' factor of volatiles is more important than has hitherto been thought.

A similar idea is evident in the recent work of C. E. SPOONER[8] and C. GEORGIADIS[9] who suggest the coordination of swelling index of coals with their volatiles. Swelling index is no doubt a good classifier of iso-vol coals having different properties, but is applicable only to bituminous coals.

As an alternative and better index of the quality of volatiles the moisture content was suggested earlier[7]. In fact, it was shown (Fig. 3 of 'Coal systematics: Part I') that *in any given range of high volatile coals* the air-dried

XUM

moisture of coals having the same percentage of volatile matter bears a linear relationship to the calorific values of their volatiles, making possible the evaluation of calorific value and elementary composition from proximate analysis.

The role of air-dried moisture in determining the calorific values of the volatiles of high volatile coals has since been further investigated and extended. It has now been observed that *irrespective of the yield of* volatiles of these coals, the air-dried moisture (at 60 per cent relative humidity) of such coals (expressed as parts of moisture per 100 parts of unit coal) is a linear measure of the calorific values of their volatiles (*Figure 1*).

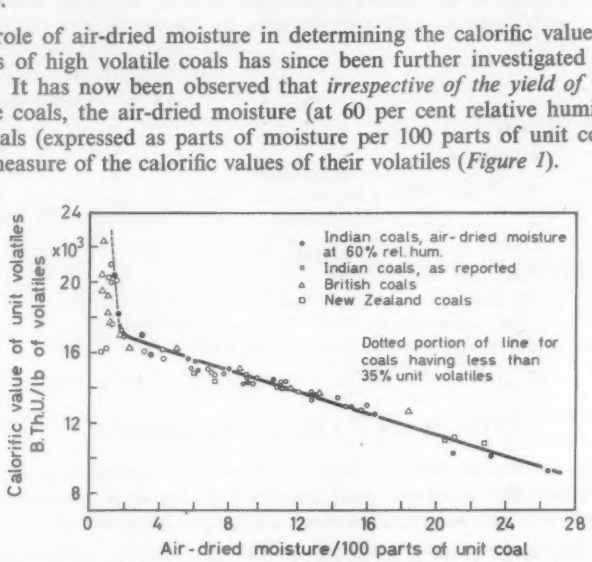

Figure 1. Relation between air-dried moisture of coals and calorific value of their volatiles

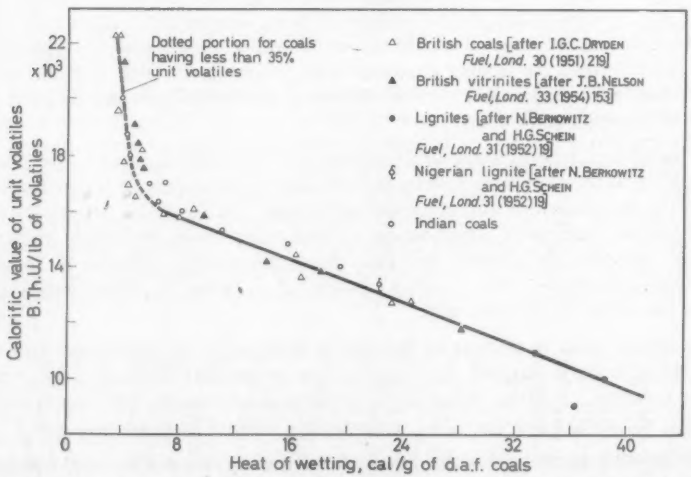
Calorific value of unit volatiles
B.Th.U./lb of volatiles
x10³
22
18
14
10
0
8
16
24
32
40
Heat of wetting, cal/g of d.a.f. coals
Dotted portion for coals having less than 35% unit volatiles
British coals [after I.G.C. Dryden Fuel, Lond. 30 (1951) 219]
British vitrinites [after J.B. Nelson Fuel, Lond. 33 (1954) 153]
Lignites [after N. Berkowitz and H.G. Schein Fuel, Lond. 31 (1952) 19]
Nigerian lignite [after N. Berkowitz and H.G. Schein Fuel, Lond. 31 (1952) 19]
Indian coals

Figure 2. Relation between heat of wetting in methanol of coals and calorific value of their volatiles

It is significant to note that the above linear relationship is true *only for the high volatile coals* (including lignite). But the relationship when extrapolated to high rank coals shows a 'break' (shown in the dotted portion of the curve). This transition point (at 35 per cent volatile matter or 85 to 86°C) between the high volatile, low rank coals and those of higher rank may be of profound significance in their structural pattern, as was indicated earlier and will be discussed elsewhere.

An exactly similar relationship has also been found to exist between the heat of wetting (in methanol) of coals and the calorific values of their volatiles (*Figure 2*).

Another relationship of the calorific values of volatiles of coals with their capacity moisture (*Figure 3*) has also been observed but the relation is not

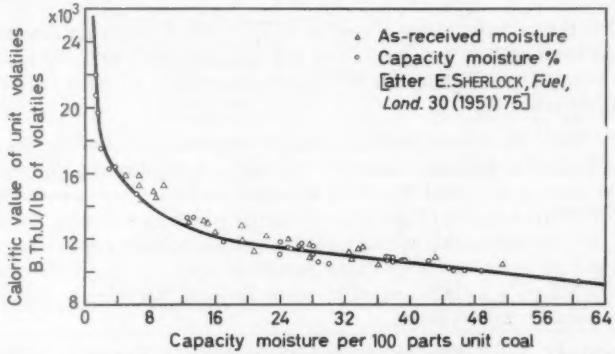

Figure 3. Relation between capacity moisture of coals and calorific value of their volatiles

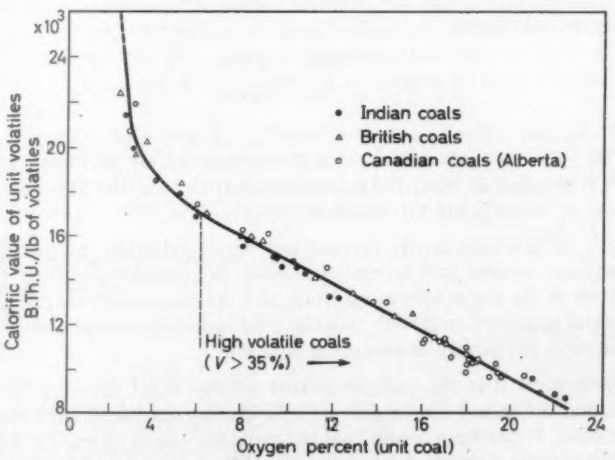

Figure 4. Relation between oxygen (unit coal) of coal and calorific value of volatiles

linear throughout the range of high volatile coals, as with air-dried moisture or heat of wetting (in methanol). These relationships, in the light of one more relation that has been found to exist between the oxygen of coal and the calorific values of their volatiles (*Figure 4*), appear to be significant and an interpretation of these is attempted elsewhere, which might throw light on the nature of moisture in coal.

Apart from the implications of the above relationships, the practical application of the parameters, e.g. moisture and heat of wetting (*Figures 1–3*), in the systematics of high volatile coals may be at once self-evident.

Thus, a direct use of the relations would be in the calculation of the calorific values of high volatile coals by the equation

$$Q = 144\,F + y.V \qquad \ldots.[1]$$

where Q is the calorific value of coal in B.Th.U./lb, V, the volatiles per cent and F, the fixed carbon per cent, all on the unit coal basis and 144 and y are factors denoting one hundredth of the calorific values of fixed carbon and volatiles respectively.

Clearly now, the whole problem can be resolved into finding the value of y, the fractional calorific values of volatiles. A solution to the problem, it will be seen, is provided by either air-dried moisture, capacity moisture, or heat of wetting values (*Figures 1–3*) any of which can directly locate the 'quality', i.e. the heat value of the volatiles of high volatile coals, *irrespective of the yield of volatiles*. The above equation may be found to meet the long-felt want of a suitable calorific value formula for high volatile coals from proximate analysis alone.

Alternatively, for convenience, the relationships in *Figures 1* and *2* may be put in the form of two linear equations in terms of air-dried moisture or heat of wetting from which the calorific values of volatiles of high volatile coals may be calculated:

$$Y = 17\,300 - 300M \qquad \ldots.[2]$$

$$Y = 17\,280 - 180\,hw \qquad \ldots.[3]$$

where Y denotes calorific value of volatiles of any high volatile coal in B.Th.U./lb, M, the per cent air-dried moisture at 60 per cent relative humidity (expressed as parts/100 parts unit coal) and hw, the heat of wetting (in methanol) in cal/g dry-ash free coal.

The role of moisture briefly pointed out here establishes the possibilities of its use as a suitable and natural parameter in coal classification. In fact on the basis of the above role of moisture and the consequent correlations of fundamental values of coal with volatiles and moisture, a coal classification chart has been tentatively drawn up as in *Table 1*.

It will be seen that the pattern is that of the A.S.T.M. classification[4]. The essential difference lies in the use of different parameters for the high volatile coals. It has been found that the moisture limits given (on the basis of formulae to be published later) for the different ranks of coal work as satisfactorily as the limits of moist mineral-matter-free calorific value adopted

Table 1. Classification of coals by rank

Class	Group	Limits of volatiles or moisture		Requisite physical properties
		Volatiles per cent (d.m.f.)	Capacity moisture per 100 parts of d.m.f. coal	
I. *Anthracite (non-agg.)*	1. *Meta-anthracite*	< 2	*Not important*	
	2. *Anthracite*	2–8	*Not important*	
	3. *Semi-anthracite*	8–14	*Not important*	*Non-agg.**
II *Bituminous (agglomerating)*	1. *Low volatile bituminous coal*	14–22	*Not important*	
	2. *Medium volatile bituminous coal*	22–31	< 3†	
	3. *High volatile A bituminous coal*	>31	1–6	
	4. *High volatile B bituminous coal*	>31	6–10·5	
	5. *High volatile C bituminous coal*	>31	10·5–16·5	*Either agglomerating or non-weathering*
III. *Sub-bituminous (non-agg.)*	*Sub-bituminous A*	>31	16·5–22·5	*Both weathering and non-agglomerating*‡
	Sub-bituminous B	>31	22·5–33·0	
	Sub-bituminous C	>31	33·0–48·0	
IV. *Lignitic (non-agg.)*	*Lignitic*	>31	48·0–100·0	*Consolidated*
	Brown coal	>31	>100·0	*Unconsolidated*

* If agglomerating, the coal is classified in low volatile group of bituminous class.
† If moisture is >3 in this group, the coals, irrespective of the volatiles limit, have to be classified in terms of moisture alone like the high volatile coals.
‡ If non-weathering or agglomerating the coal is placed in 'high volatile C' bituminous coal.

by the A.S.T.M. Similarly, air-dried moisture (at 60 per cent relative humidity) limits for the proposed classification system have also been developed. Details are being published in a series of papers[7] entitled 'Coal Systematics'.

The author gratefully acknowledges his indebtedness to Dr J. W. Whitaker, former Director, Central Fuel Research Institute, and to the present Director, Dr A. Lahiri, for their keen interest and help in the work.

B. K. MAZUMDAR

Central Fuel Research Institute,
Jealgora, Bihar,
India

(*Received June 1957*)

REFERENCES

[1] GOUTAL, M. *C.R. Acad. Sci., Paris* 135 (1902) 477
GOUTAL, M. *J. Soc. chem. Ind., Lond.* 21 (1902) 1267
[2] PARR, S. W. *J. industr. Engng Chem.* 14 (1922) 919
PARR, S. W. *Bull. Univ. Ill. No. 180* (1928) 116
[3] MOTT, R. A. *J. Inst. Fuel* 22 (1948) 2

XUM

[4] 'Specification D 388–38', *Book of Standards*, Pt III, p1. American Society of Testing Materials: Philadelphia, 1939
[5] SEYLER, C. A. *Proc. S. Wales Inst. Engrs* 21 (1899) 483; 22 (1900) 112; 47 (1931) 547; 53 (1938) 254
[6] MAZUMDAR, B. K., BHANGALE, P. H. and LAHIRI, A. *Fuel, Lond.* 36 (1957) 307
[7] MAZUMDAR, B. K. *J. sci. industr. Res.* B13 (No. 12) (1954) 857
[8] SPOONER, C. E. *Fuel, Lond.* 30 (No. 9) (1951) 193
[9] GEORGIADIS, C. *J. Usin. Gaz.* 76 (No. 9) (1952) 314

The Action of Alkalies on Low-rank Coals

THE action of alkalies on coals, under comparatively mild conditions, has been studied by several workers [1–6], who have in general found some increase in the content of reactive oxygen-containing groups or in the solubility in benzene–alcohol or alcoholic alkalies. Other workers[7] have found that by the action of aqueous alkali at temperatures close to those of thermal decomposition a sub-bituminous coal is converted to a mixture of phenols, bases, and neutral oils. These changes have been attributed mainly to hydrolytic action.

The present authors have found that the treatment of brown and sub-bituminous coals with alcoholic or aqueous alkali at about 190°C for about 12 hours followed by acidification produces materials which are almost entirely soluble in alcohol or pyridine and which fuse on pyrolysis to give coherent swollen cokes in a crucible test. The original coals were non-agglomerating when pyrolysed under these conditions.

Table 1. Analytical results of coals and reaction products
(All results on d.a.f. basis)
Reaction with alkali in ethanol

Constituent	*MORWELL*		*YALLOURN NTH*		*MUJA*	
	Orig.	*Product**	*Orig.*	*Product**	*Orig.*	*Product**
Ash, air dried (%)	4·3	0·3	3·4	0·1	2·9	0·3
Carbon (%)	70·2	72·6	68·6	68·8	75·2	78·5
Hydrogen (%)	4·9	6·3	5·0	6·2	4·2	7·4
Nitrogen (%)	0·6	0·5	0·6	0·5	—	—
Sulphur (%)	1·0	0·7	0·3	0·2	—	—
Oxygen (% *by difference*)	23·3	19·9	25·5	24·3	—	—
Product—yield (%)	77·0		80·0		60·0	
Total acidity (mequiv./g)	6·4	6·4	7·6	7·7	4·7	3·4
Carboxyl† (mequiv./g)	1·2	0·8	1·4	1·0	1·5	0·4
Methoxyl† (mequiv./g)	0·2	0·6	0·4	0·6	—	—
Carbonyl‡ (mequiv./g)	2·1	2·1	2·3	2·3	—	—
Volatile matter (%)	—	—	50·0	55·2	39·2	69·8

* Alkali-soluble, precipitated by acid.
† Some esterification is known to have taken place during isolation of the product.
‡ Tentative values only.

The ultimate analyses of the products show a marked increase in hydrogen and some decrease in oxygen, but the content of reactive functional groups remains virtually unaltered. Besides the results quoted in *Table 1* it was also found that both the original and treated coals contain a small amount of alcoholic hydroxylic groups. The methods of determining the functional groups have been described elsewhere[8]. It must be concluded that the reaction

involved is not one of simple hydrolysis since no new functional groups have appeared. Treatment of low-rank coals with alkalies causes no marked changes in their i.r. spectra, apart from an increase in absorption at about 2900 cm^{-1}, corresponding to a C—H stretching vibration, and some slight decrease in the 1600 cm^{-1} region. The molecular weights of some of the reaction products, determined by the ebullioscopic method, were found to be in the range of 500 to 1000. Measurement of loss of weight during heating to 800°C with a thermobalance showed that the thermal behaviour of an alcohol-soluble reaction product was similar to that of the coal from which it had been obtained.

A Muja (Western Australian) coal containing 48 per cent opaque petrographic constituents did not dissolve completely after treatment with alkali in *iso*propyl alcohol. The alcohol-insoluble residue dissolved partially in pyridine and both the soluble portions possessed coking properties. Analyses of the products are given in *Table 2*.

Table 2. Analytical results of coals and reaction products. Reaction of Muja coal with alkali in isopropanol

	Ash (air dried)	*Carbon* (*d.a.f.*)	*Hydrogen* (*d.a.f.*)
Original coal	2·9	75·2	4·2
Alcohol-soluble material	0·2	88·1	7·8
Pyridine-soluble material	0·4	79·2	5·7
Pyridine-insoluble material	1·3	80·8	4·2

Other coals with carbon contents of less than 80 per cent yielded considerable amounts of pyridine-soluble material when treated in a similar manner. The soluble portions were found to possess coking properties.

The materials obtained by treatment of low-rank coals with alkalies are in a much more suitable form than the original coals for the investigation of their chemical structure by hydrogenation, oxidation, or determination of functional groups. The examination, now in progress, of such materials should advance the study of the chemical mechanism of coke formation, especially the effect of molecular weight and functional groups on coking properties.

J. D. BROOKS and S. STERNHELL

Commonwealth Scientific and Industrial Research Organization,
Coal Research Section,
P.O. Box 3,
Chatswood, New South Wales

(*Received August 1957*)

REFERENCES

[1] BERKOWITZ, N. *Nature, Lond.* 162 (1948) 960
[2] ERASMUS, P. *Über die Bildung und den chemischen Bau der Kohlen*, p 10. F. Enke: Stuttgart, 1938

XUM

[3] ZABAVIN, V. I., KLEIMANOVA, L. F. and SURKOVA, V. L. *Trud. Inst. gor. Iskop.* 5 (1955) 48
[4] IHNATOWICZ, A. *Komun. No. 125*, p 3. Prace Głównego Instytutu Górnictwa: Katowice: 1952
[5] KRÖGER, C., POHL, A., KUTHE, F., HOVESTADT, H. and BÜRGER, H. *BrennstChemie* 38 (1957) 33
[6] HOWARD, H. C. *Chemistry of Coal Utilization* (Ed. LOWRY, H. H.), Chap. 11. J. Wiley: New York, 1945
[7] PARKER, F. G., FUGASSI, J. P. and HOWARD, H. C. *Industr. Engng Chem.* (*Industr.*) 47 (1955) 1586
[8] BROOKS, J. D. and STERNHELL, S. *Austral. J. appl. Sci.* In press

Reduction of Coal by Lithium–Ethylenediamine

STUDIES on coal structure have been hampered by the lack of a method for reduction of coal at low temperatures. Many organic substances, including lignin, are reduced[1] by metals in liquid ammonia; however, the insolubility of coal in ammonia renders this reagent useless. It was therefore decided to investigate a related system, lithium in ethylenediamine. This is a powerful reducing agent[2], being very effective in reducing phenols and polycyclic aromatic hydrocarbons; and it incorporates a good coal solvent. This report gives preliminary results on the reduction of four coals and the pyridine-soluble extract of one of them.

Bruceton anthraxylon (8·00 g) in anhydrous ethylenediamine (400 ml) was treated with lithium (18·00 g) at 90 to 100°C during 2½ hours. Addition of water (1000 ml) and centrifugation gave fraction A, which was washed by centrifugation until the washings were neutral. The supernatant liquid was distilled to small volume to remove most of the ethylenediamine and the residue (fraction B) washed by centrifugation.

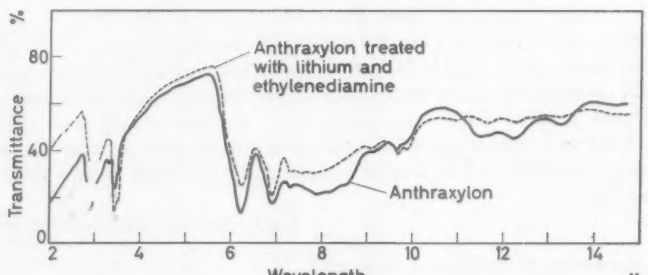

Figure 1. Infra-red spectra of Bruceton anthraxylon, and of fraction A obtained from the reduction with lithium and ethylenediamine

The i.r. spectrum (*Figure 1*) of fraction A (2·52 g) showed increased C—H absorption at 3·45μ; decreased absorption at 8·0μ (phenoxy structures); and a decrease in intensity of the so-called 'aromatic' bands at 11·5μ, 12·3μ, and 13·3μ of about 90 per cent. The 6·25μ band was no longer the most prominent band in the spectrum, as it is in anthraxylon. Fraction B (4·68 g) showed similar changes in its i.r. spectrum.

Since the reduction results in the formation of the $H_2NCH_2CH_2NHLi$ amide, which is known[3] to cause isomerization and dehydrogenation, it was necessary to compare the results of lithium reduction with those of amide treatment. It was found that the i.r. spectrum of the anthraxylon was not changed by treatment with the amide. The alterations in i.r. spectra in the experiments using metallic lithium are thus to be attributed to reductive processes.

The i.r. spectra of Wyoming coal and West Virginia coal reduced with lithium and ethylenediamine according to the same procedure used for anthraxylon showed changes similar to those observed for Bruceton anthraxylon. Reduction of a pyridine extract of Wyoming coal (comprising 13 per cent of the coal) gave the i.r. spectrum shown in *Figure 2*. The changes are similar to, but more marked than, those shown by anthraxylon.

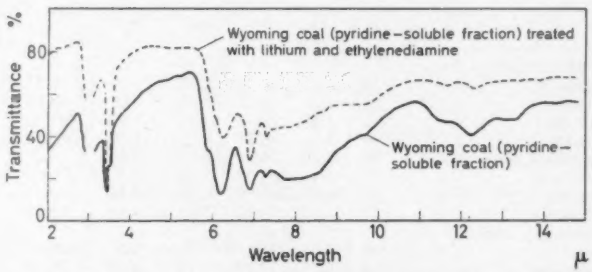

Figure 2. Infra-red spectra of pyridine-soluble fraction of Rock Springs coal before and after treatment with lithium and ethylenediamine

The u.v. and visible spectrum of anthraxylon has been determined on thin sections and on potassium bromide pellets[4]. The intensity of absorption of the reduced material was decreased to an average value of 40 per cent when compared with the starting anthraxylon; the absorption intensity of the material treated with the amide $H_2NCH_2CH_2NHLi$ was decreased to an average value of 75 per cent. A large part of this change may be caused by decreased scattering of the particles of the reduced material; however, the decrease in absorption is probably significant. The decrease in absorption may be attributed to a decrease in the amount of conjugated double bonds (mainly carbon–carbon conjugated double bonds and aromatic structures) or to a decrease in the amount of free radicals present. The reduced anthraxylon was brownish in colour, whereas the starting material was black.

Anthracite (2·00 g) and ethylenediamine (200 ml) were heated at 115°C for two hours, to allow any slow softening or swelling to take place. Then lithium (15·00 g) was added at 115°C during 2 hours. Water was added and the precipitate centrifuged and washed by centrifugation until the washings were neutral. The recovered material weighed 2·15 g. Anthracite does not have a satisfactory i.r. spectrum, so that it became necessary to determine the amount of hydrogen taken up by the coal. However, since coal absorbs a considerable amount of ethylenediamine which cannot be removed by washing or acidification, the analytical data must be corrected to calculate the amount of hydrogen added. This correction was made according to a modification,

XUM

to be described in detail later, of the calculation of I. G. C. DRYDEN[5]. It is assumed here that all of the nitrogen in the coal is retained in the reduction, and that the increase in nitrogen in the reduced sample is caused by absorption of ethylenediamine molecules as such; it can be shown that these assumptions are not critical. *Table 1* shows that the actual hydrogen uptake for the materials studied ranges from 0·7 to 2·3 per cent.

Table 1. Hydrogen uptake of coals

Substance	*Ultimate analysis of dried sample, per cent*				*Ultimate analysis calculated on ash- and ethylenediamine-free basis, per cent*		*Hydrogen uptake, per cent*
	Ash	H	C	N	H	C	
Bruceton (Pittsburgh) anthraxylon	2·36	5·26	81·39	1·41	5·39	83·35	
ditto, reduced	2·61	7·26	78·22	4·30	7·03	83·16	1·64
Anthracite coal	3·92	1·88	90·13	0·78	1·97	93·80	
ditto, reduced	2·93	3·56	86·37	2·42	3·29	90·85	1·32
Wyoming (Rock Springs) coal	1·93	5·44	74·54	1·65	5·55	76·01	
ditto, reduced	3·48	6·45	69·67	3·93	6·31	74·00	0·76
West Virginia (Big Knob) coal	7·09	4·83	80·79	1·20	5·20	86·95	
ditto, reduced	5·87	6·44	79·21	2·30	6·67	85·25	1·47
Wyoming coal, pyridine extract	1·01	6·25	78·11	1·33	6·31	78·91	
ditto, reduced	1·95	8·75	77·22	3·79	8·65	81·10	2·34

There is no doubt that lithium–ethylenediamine is an effective reagent for the reduction of coals. The relation of hydrogen uptake to rank of the starting coal, and work on the constitution of the reduced material, will be reported later.

This work was carried out as part of a cooperative agreement between the U.S. Bureau of Mines and the Union Carbide Corporation.

L. REGGEL, R. RAYMOND,
S. FRIEDMAN, R. A. FRIEDEL and I. WENDER

Central Experiment Station,
Bureau of Mines, Region V
U.S. Dept of the Interior
Bruceton, Pa

(*Received September 1957*)

REFERENCES

[1] SEMECHKINA, A. F. and SHORYGINA, N. N. *Zh. obshch. Khim., Mosk.* 23(1953) 617 and 1673
[2] REGGEL, L., FRIEDEL, R. A. and WENDER, I. *J. org. Chem.* 22 (1957) 891
[3] REGGEL, L., FRIEDMAN, S. and WENDER, I. *Abstracts* of Papers, 129th Meeting, American Chemical Society, Dallas, Texas, April 1956, p 10N
[4] FRIEDEL, R. A. *Nature, Lond.* 179 (1957) 1237; unpublished work
[5] DRYDEN, I. G. C. *Fuel, Lond.* 30 (1951) 145